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SE AND VOLUMETRIC BEHAVIOR IN THE CARBON DIOXIDE - HYDROGEN SULFIDE SYSTEM

by

C. A. Makrygiorgos

December, 1958.

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THE UNIVERSITY OF ALBERTA

PHASE AND VOLUMETRIC BEHAVIOR IN THE METHANE-CARBON DIOXIDE-HYDROGEN SULFIDE SYSTEM

A Dissertation
submitted to
The Faculty of Graduate Studies
in Partial Fulfilment
of the Requirements for the Degree
of Master of Science in Chemical Engineering

Department of Chemical and Petroleum Engineering

by

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Edmonton, Alberta

December, 1958.

ABSTRACT

In the first part of this work, the isobaric-isothermal loop of the methane-carbon dioxide-hydrogen sulfide system at the pressure of 1330 PSIA and temperature of 160°F. was investigated, in an effort to complete the work done on the phase behavior of the above system at the mentioned temperature.

The experimental procedure consisted of preparing a known mass of gas mixture, of definite composition, with subsequent compression of the system to the two phase region. Experimental phase composition determinations were carried out defining thus, the three component two phase region.

The experimental data were correlated by means of calculation of equilibrium ratios for the pure components, and the deviation from ideality for the liquid and gas phases was illustrated by means of activity coefficient calculations.

Comparison of the experimental results obtained to those calculated through the use of experimental data on the same system at some other pressures and temperature of 160°F., indicates substantial differences.

In the second part of this work the volumetric behavior of several methane-carbon dioxide-hydrogen sulfide mixtures was investigated at temperatures of 160°, 100° and 40°F. and pressures up to 3000 PSIA. Three carbon dioxide-hydrogen

sulfide binary mixtures were also investigated at the temperature of 160°F. and pressures up to approximately 2000 PSIA.

The technique employed consisted of preparing, in the gas phase, a mixture of known composition with subsequent compression and recording of the variables, i.e., pressure, temperature and volume. Correlation of the experimental data was achieved by calculating compressibility factors for the mixtures at each temperature as well as residual volumes.

The experimental results indicate that for the higher temperatures the compressibility of the mixtures can be relatively accurately described by means of the pure components using methods reported in the literature. Some of the prediction methods fail to describe the compressibility even at the higher temperatures. For the lowest temperature of 40°F. where even at low pressures carbon dioxide and hydrogen sulfide are in their two phase region there is no adequate method of describing the system's behavior.

It should also be mentioned that greatest discrepancies occur for mixtures poor in methane content.

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LIST OF SYMBOLS

a - activity of a component in a solution.

γ - activity coefficient.

γ' - activity coefficient ratio.

c - component in a system.

C - composition parameter defined as the mole fraction of carbon dioxide in the vapor phase to the sum of the mole fraction of methane and carbon dioxide in the vapor phase.

F - degrees of freedom of a system or number of variables of the system.

f - fugacity of a pure component.

$\bar{f}$ - fugacity of a component in a solution.

f^* - fugacity of a pure component at its own vapor pressure at the temperature of the system.

f_P - fugacity of a pure component at a pressure equal to the system pressure.

K - equilibrium ratio.

n - number of moles of a component in the gas phase.

p - partial pressure of a component in the vapor phase.

P - total system pressure (absolute).

R - universal gas constant.

T - absolute temperature in degrees Rankin.

V - total or molal volume in gas phase.

$\bar{V}$ - volume of a unit weight of a gas.

ϕ - number of phases.

LIST OF SYMBOLS (CONTINUED)

ϕ_1 - the reciprocal of the slope of the isometric of a gas as defined in the text.

ϕ_2 - the internal pressure of a gas as defined in the text.

X,x - mole fraction of a component in the liquid phase.

Y,y - mole fraction of a component in the vapor phase.

Z,z - compressibility factor in the gas phase.

α - residual volume.

Subscripts

L - referring to liquid phase.

V - referring to vapor phase.

i - referring to any component.

GENERAL INTRODUCTION

The past twenty-five years in petroleum production and processing have seen a broadening in the range of operating temperatures and pressures. To produce and process hydrocarbon mixtures efficiently at these varied conditions has required the extensive efforts of many researchers to accumulate and correlate basic vapor-liquid equilibrium data.

Similarly, all petroleum engineering problems use the PVT behavior of fluids in one form or another. Gas reserves, gas pressure gradients in well bores, and the calculation of gas flow rates at the surface are three example problems requiring a knowledge of gas behavior.

An accurate knowledge of the fluid density is also required in the calculation of orifice meter correction factors in the metering of high pressure gases, the times of contact of vapors in a cracking furnace, and the vapor velocities in bubble towers.

Finally, the tendency for condensation of some non-hydrocarbon compounds such as carbon dioxide and hydrogen sulfide - present in a variety of natural hydrocarbon mixtures - which is favored by the conditions during the refining operations, necessitates an adequate knowledge of phase and volumetric behavior for these mixtures.

Although phase equilibrium and compressibility factor measurements of numerous binary systems, containing a paraffin hydrocarbon and carbon dioxide or hydrogen sulfide, have been published, there is only a limited number of papers dealing with the ternary system.

The work of J. A. Bailey (1) and A. P. Lorenzo (2) at the University of Alberta has contributed to the phase equilibrium study of the methane-carbon dioxide-hydrogen sulfide system, at three temperatures and several pressures up to 1800 PSIA.

The aim of the present work is to complete the investigation of the above ternary system by determining its isobaric-isothermal section at 1330 PSIA and 160°F., and to study the volumetric behavior of the system in the single (vapor) phase region at various compositions, temperatures of 40, 100 and 160°F. and pressures up to 3000 PSIA.

PART I. PHASE BEHAVIOR OF THE METHANE-CARBON DIOXIDE-HYDROGEN SULFIDE SYSTEM AT 160°F. AND 1330 PSIA.

A. INTRODUCTION

The primary purpose of the first part of the investigation was to extend the study of the methane-carbon dioxide-hydrogen sulfide phase behavior relationship begun by J. A Bailey and A. P. Lorenzo.

It was felt that for the completion of the system at the temperature of 160°F., an additional isobaric section at a pressure in the neighborhood of 1300 PSIA should be studied. The reason was an uncertainty as to the shape of the K vs P curves for each of the three components at the mentioned pressure region. It should be mentioned here that A. Lorenzo covered the isothermal-isobaric section at 160°F. and 1300 PSIA by employing prediction methods, utilizing data at some other pressures and the temperature of 160°F.

No modifications of the existing apparatus were made and the same general experimental technique and sampling methods, followed by Bailey and Lorenzo, were used.

The data were analyzed and compared to the figures calculated by Lorenzo for the predicted isothermal-isobaric section of 160°F. temperature and pressure of 1300 PSIA.

B. SOME THEORETICAL ASPECTS ON THE PHASE BEHAVIOR OF A MULTICOMPONENT SYSTEM

1. Historical Consideration

Early investigators discovered that at relatively low pressures, mixtures obeyed relatively simple rules, e.g., Dalton's and Raoult's laws combined: K = vapor pressure divided by total pressure, and therefore prediction of vaporization ratios for hydrocarbons was generally believed to be a simple matter, i.e., $K_i = Y_i/X_i$.

Later investigators discovered that at high pressures additional considerations were required for predicting vaporization ratios, e.g., K's defined in terms of pure component fugacities which gave good results up to several hundred PSIA. Both types of K's were, by definition, independent of composition. That is, for a given component, K the equilibrium ratio Y/x, was defined as a function of temperature and pressure only.

Still later investigators learned how these simple rules actually break down progressively with increasing pressure, and become totally inadequate at pressures approaching the critical pressure. At these pressures K values apparently depend to a large degree on composition as well as temperature and pressure; that is, the K's for

any component depend also upon the presence and the amounts of the other constituents in the mixture.

Also, pronounced effects on K-values were noted in systems containing compounds differing from the paraffins in molecular structure, such as aromatic, as well as non-hydrocarbons, such as alcohols, H_2S, CO_2, N_2, etc. In short, K-values are not constant but vary for each component depending on temperature, pressure and composition of the mixture.

To obtain quantitative information related to the effects of composition on K-values, numerous studies were made covering the entire two phase regions of various binary hydrocarbon systems, of several ternary mixtures and some more complex mixtures. In each case, a pronounced effect on K-values was measured as the mixture approached its critical conditions. Many attempts were then made to define quantitatively this radical departure from ideal liquid and vapor behavior. One approach was to define vapor-liquid behavior in terms of thermodynamic relationships and PVT behavior of pure components. Such attempts are the arbitrarily derived equations of Van Laar and Margules.

This approach which has promise of a high degree of accuracy is impractical for routine calculations. A second approach was to utilize the large volume of directly measured vapor-liquid equilibrium ratios which has accumulated. This approach makes use of the concept of convergence pressure to describe the influence of composition on equilibrium ratios.

However the greater part of this information has been collected for binary hydrocarbon systems, whereas the primary need has been, and is, for vaporization ratios of hydrocarbons in multicomponent systems and mixtures containing non-hydrocarbon compounds. Therefore, although an extensive experimental program for a multicomponent system is time-consuming, it is the best means now available for the determination of phase equilibrium.

2. Three Component Phase Equilibrium

The methods of representing the ternary system graphically are sufficiently different to warrant more explanation than is necessary for the binary system. The phase rule statement of the equilibria which may exist in a ternary system is summarized in the following formula:

$F = 3 + 2 - \phi = 5 - \phi$ where F the degrees of freedom of the system and ϕ the number of phases.

For a single phase system, when $F = 4$, i.e., temperature, pressure and two compositions, various methods have been proposed to represent the composition of ternary-isobaric systems which are based on the triangle, but only two have been used to appreciable extent.

Since phase equilibrium measurements are mostly carried out under isothermal conditions, the temperature is selected as the invariant quantity. Then a three dimensional representation of the phase equilibrium can be acoomplished by selecting pressure as the ordinate and two compositions as abcissas. The so-constructed three dimensional model can be studied as a number of parallel planes - isobaric sections, of the form of an equilateral triangle.

The first method proposed by Gibbs (3), makes use of an equilateral triangle of unit altitude. The quantities of the components are expressed as fractional parts of the whole; the sum of the fractional parts is therefore equal to unity.

The corners of the triangle represent the pure components. A point on the side of the triangle represents the composition of a binary system, and a point within the triangle represents a composition of the ternary system.

The second method, due to Roozeboom (3), has found greater usage. An equilateral triangle is used but the length of the side is made equal to unity. The composition of a ternary system is determined by this method, by the distances to the sides in a direction parallel to the sides, in distinction from the first method where the perpendiculars from the vertices to the sides are used. Some useful features of the triangle, whether equilateral or not, should be noted:

1. The ratio of two components is constant along a line through the third. The composition of a point then may be expressed either in terms of %A and %B (any two components) or in terms of %C and the ratio A/B as the independent composition variables.
2. The ratio of A to any fixed composition such as D on the opposite side is similarly constant along a line through either of the other corners. This principle can be extended whenever necessary or convenient for a sub-triangle in the actual ABC triangle.
3. If two complexes or compositions are mixed, the total composition lies on the line joining them, at a point dividing that line into segments inversely proportional to the ratio of the quantities of the original complexes taken.

Some of the above properties are used in a graphical construction of the equilibrium loop from experimental data relative to an arbitrarily chosen composition parameter C, as is explained in Lorenzo's and Bailey's works.

It is worthy of note that each side of the as above formed isothermal prism, represents the pressure composition loop for one of the binaries; that bubble and dew sections are represented by two different surfaces inside the prism; that the composition of any two coexisting phases are represented

by straight tie-lines and that single phases are represented by solid portions within the prism since they possess three degrees of freedom.

3. The "Ideal Solution", "Fugacity", and "Activity Coefficient" and their Application to the Behavior of "Real" Systems.

The distribution of a component of a system between vapor and liquid is expressed by the equilibrium constant K. The equilibrium constant is defined as the ratio of the mole fraction of the component in the vapor phase Y, to the mole fraction of the component in the liquid phase x.

There are several methods that can be used to evaluate K.

Raoult's law and Dalton's law may be combined to calculate concentration of each component in the vapor and liquid phase.

Raoult's law and Dalton's law may be expressed as follows:

$$p = x \cdot p^* \quad \text{(Raoult's law)}$$

$$p = y \cdot P \quad \text{(Dalton's law)}$$

where p = partial pressure of the component in the vapor phase as defined by Dalton or Raoult.

p*= vapor pressure of the component at the temperature of the system.

P = total pressure of the system.

x,y = mole fraction of the component in the liquid and vapor phases.

Combining the equations of these two laws we have: $xp^* = yP$ which can be arranged to give: $\frac{p^*}{P} = \frac{y}{x} = K$ where, K is the equilibrium ratio at the particular temperature and total pressure. Two factors that restrict the use of equilibrium constants calculated by Raoult's and Dalton's laws are immediately apparent:

(1) A pure compound cannot have a vapor pressure at temperatures above its critical temperature. Thus, Raoult's law is limited to temperatures less than the critical temperature of all of the compounds in the system.

(2) Dalton's partial pressure law assumes that each component in the vapor phase behaves as an ideal gas. For practical purposes, the ideal gas assumption places an upper limit of pressure of 50 to 100 PSIA.

A better approximation of actual equilibrium constants is obtained by defining the constants in terms of the fugacities of the compounds. The fugacity may be looked upon as a vapor pressure modified to represent correctly the escaping tendency of the molecules, from one phase into the other. By using fugacities to define equilibrium constants, the departure of the vapor from the ideal gas behavior, and the effect of the total system pressure on the vapor pressure of the components, are taken into account.

In an ideal solution the fugacity of any component in the system is equal to the fugacity of the component in the pure state times its mole fraction. This is frequently referred to as the Lewis and Randall rule.

Thus if $\bar{f}_L$ and $\bar{f}_V$ are the fugacities of a component in the liquid and vapor phases respectively and f_L and f_V in the pure states

$$\bar{f}_L = f_L \cdot x \text{ and } \bar{f}_V = f_V \circ y$$

At equilibrium conditions the fugacities of the components are equal in the liquid and vapor phase, so that (eq. 1) $\frac{y}{x} = \frac{f_L}{f_V} = K$ (ideal). Ideal constants are limited by one important fact:

At a given temperature a compound can exist as a single phase at any pressure other than the vapor pressure, so that the fugacity of either the vapor or liquid (depending upon whether the pressure is greater or less than the vapor pressure of the component) must be obtained by extrapolation of the fugacity pressure relationship.

To obtain numerical values for f_V and f_L to use in relation (1) one has to integrate graphically the relation:

$$\ln \frac{f_P}{f^*} = \frac{1}{RT}\int_{P^*}^{P} VdP \qquad \text{(eq. 2)}$$

that is integrate the specific volume-pressure curve from the

vapor pressure p* to the operating pressure P at the fixed temperature of the mixture.

As the above mentioned extrapolation is somewhat arbitrary the farther the system pressure is from the vapor pressure, the more uncertain the equilibrium constant becomes. Usually the ideal equilibrium constants are considered undependable at pressures more than twice the vapor pressure of the compound. For this reason, they have limited usefulness for calculations dealing with petroleum reservoir conditions.

In considering the behavior of a "real" solution, it is more convenient to use the activity, activity coefficient and activity coefficient ratio concepts. Lewis and Randall defined the activity of a component in the vapor phase of a system as the ratio of the fugacity of the component in the vapor phase over the fugacity of the pure component at the temperature and total pressure of the system and, also, the activity of the same component in the liquid phase, as the ratio of the fugacity of the component in the liquid phase over the fugacity of the pure component as a liquid at the system temperature and the corresponding vapor pressure of the component in the system.

In a mathematical form these two expressions are:

$$a_V = \frac{\bar{f}_V}{f_P} \quad \text{(eq.3) and} \quad a_L = \frac{\bar{f}_L}{f^*} \quad \text{(eq.4)}$$

Dividing equation (3) by the mole fraction in the vapor phase, we obtain the activity coefficient of the component in the vapor phase of the system: $\gamma_V = \frac{a_V}{y}$. (eq. 5) Dividing equation (4) by the mole fraction in the liquid phase, etc., we obtain the activity coefficient in the liquid phase $\gamma_L = \frac{a_L}{x}$. (eq. 6)

The ratio of $\frac{\gamma_L}{\gamma_x} = \gamma'$ (eq.7) is the activity coefficient ratio. Substituting values of γ_L and γ_V from (eq.6) and (eq.5) into (eq,7) we obtain:

$$\frac{\bar{f}_L}{x f^*} : \frac{\bar{f}_V}{y f_P} = \text{ or } \frac{y}{x} = K = \gamma' \cdot \frac{f^*}{f_P} \text{ since}$$

at equilibrium we have $\bar{f}_L = \bar{f}_V$. Apparently, γ' represents a correction factor for the deviation from the real behavior, when the fugacity method is applied in the determination of K.

C. EXPERIMENTAL TECHNIQUES

The lack of data in phase Equilibrium is primarily due to the difficulty in the construction and operation of equipment which is sufficiently adequate to yield quantitative phase data. Although equations are available to predict the composition of phases existing at equilibrium, they are limited in scope by assumptions employed in their derivation.

Experimental data are also required to determine constants in the equations for a particular system. Therefore, although an extensive experimental program for a given system is time-consuming it is the best means now available for the determination of phase equilibrium.

Although the aims of contemporary research in the field of phase behaviour are similar, the types of equipment in use differ considerably. The ultimate purpose of each however, is to facilitate the control and measurements of the primary phase variables such as, pressure, temperature and phase composition.

Scheeline and Gilliland (5) clearly state the basis for two common methods and point out the features of each.

1. THE CONSTANT VOLUME TECHNIQUE

In this method the mixture of hydro carbon is introduced into a high-pressure bomb, which can be placed bodily in a thermostatically controlled bath of any desired temperature. The apparatus is equiped with a stirring or shaking device,

vapor and liquid sampling lines, and temperature and presure indicators. Agitation is continued until equilibrium between the phases is reached, at which time samples of liquid and vapor are with drawn and analyzed. The method suffers from a number of drawbacks which tend to complicate the apparatus. It is essential that two phases be present at equilibrium, therefore the correct amount of each component must be added to the bomb at the beginning of the run and some level indicating device is necessary. As critical conditions are approached and vapor and liquid properties become similar, it is difficult to control and measure the phase interface. In order to prevent pressure reduction and corresponding flashing of liquid when samples are withdrawn, it is necessary either to isolate the two phases in separate compartments of the bomb or to add an inert substance (usually mercury) as the sample is taken, which is equal in volume to the hydro carbon removed. In order to ensure the equilibrium, agitation must be prolonged and thorough, but provisions must be made for preventing liquid droplets from entering the vapor sampling line.

2. THE VARIABLE VOLUME TECHNIQUE

The second method consists of obtaining the dew point and bubble point curves of a number of prepared samples of known composition. This can be done either by observing a

break in a plot of temperature vs pressure for a given sample or by enclosing the sample in a thick-walled quartz tube in a thermostat and observing the pressure at which the first trace of vapor or liquid appears. By cross-plotting such dew and bubble point data, points are found at which saturated liquid and saturated vapor of different compositions exist at the same temperature and pressure. Such points indicate phase equilibrium. One advantage of the method is that it conveniently gives valuable data on specific volumes, however a number of serious drawbacks limit its general usefulness.

The material used must be carefully purified and free in particular from traces of fixed gases, for in the critical region the saturation pressure is quite sensitive to small amounts of air etc. Furthermore an extremely large amount of experimental work must be done in order to define completely and accurately the phase equilibrium over all values of concentration. The most serious limitation of the method, however, lies in the fact that it can be used only for systems of two components. In more complex systems it follows from the phase rule that composition is not a unique function of P and T and that therefore dew and bubble point measurements alone cannot define the composition of two phases in equilibrium.

3. The Experimental Equipment and Technique

The apparatus employed was the one constructed by J. A. Bailey as it had been modified later by A. P. Lorenzo for his work. It is a modification of the apparatus Professor D. L. Katz of the University of Michigan used for the phase study of the carbon dioxide-methane system (6).

It is a variable volume apparatus with the principal unit being the visual type equilibrium cell adapted from a Jerguson liquid level gauge.

A similar cell was employed for the measurement of the desired amounts of the single components added. Pressure changes were made by the use of a hand-operated mercury pump and electric coils, in the air bath surrounding the equilibrium cell, provided the necessary heating of the sample to the desired temperature. An electronic relay in connection with an on-off thermoregulator held the temperature constantly at the desired level.

Pressures were recorded on a Heise pressure gauge and temperatures were measured by the use of copper-constantan thermocouples. The withdrawl of the gas phase after equilibrium had been achieved was made at constant pressure by mercury replacement of the gas leaving the cell. Collection of the gases in a sample collector followed the withdrawl and from there the samples were taken to be analyzed.

After the gas phase was entirely removed from the equilibrium cell, the pressure in the cell was lowered so that total evaporation of the remaining liquid phase would be achieved. The obtained vapor was then analyzed by employing the same technique as for the gas sample.

The Tutweiler burette was used for the determination of hydrogen sulfide content, and the Orsat apparatus for the methane content.

Figure I shows a schematic sketch of the apparatus used.

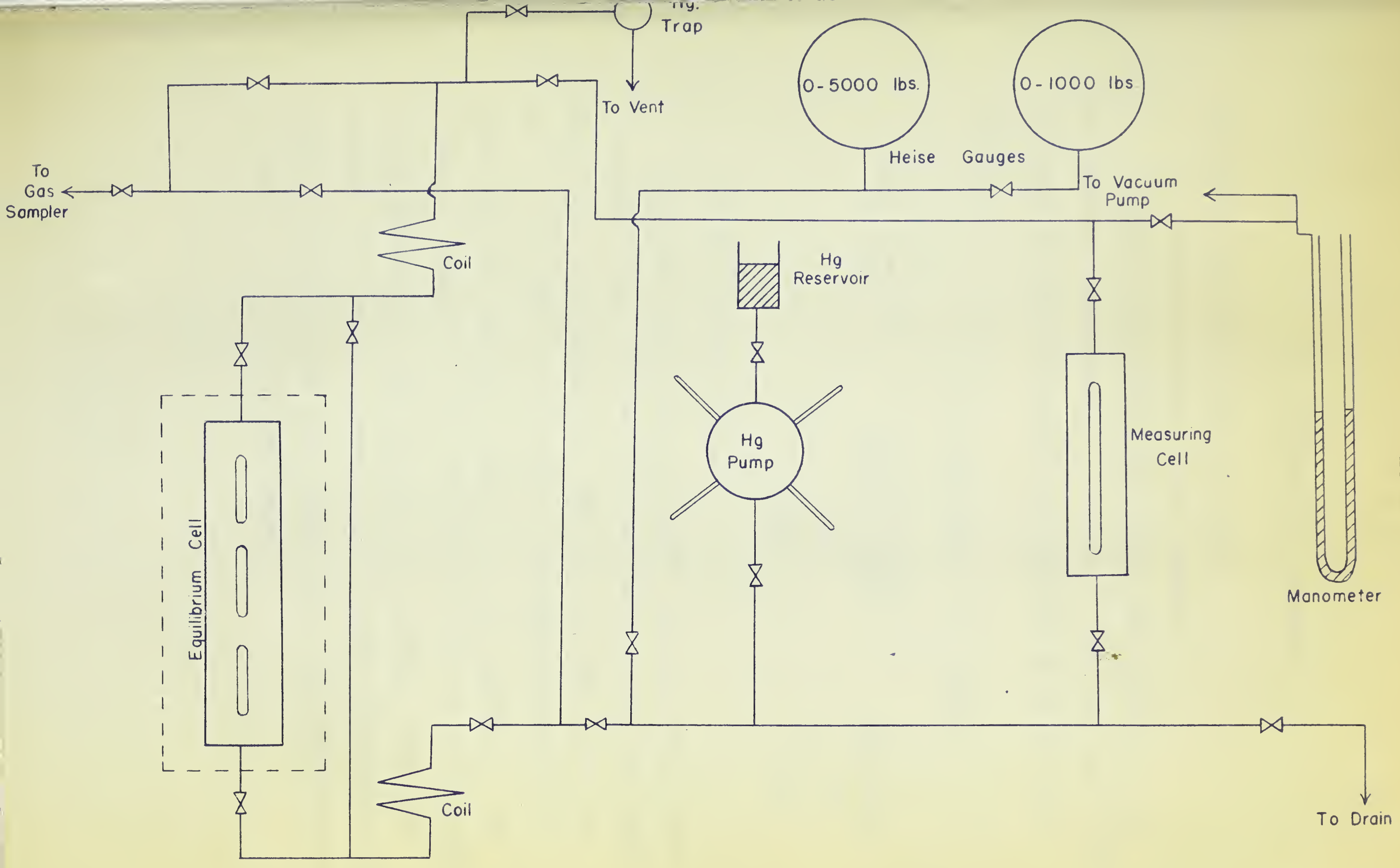


FIG. I. SCHEMATIC APPARATUS ASSEMBLY

D. EXPERIMENTAL RESULTS

(1) Phase equilibrium data at 160°F.

(a) Methane-hydrogen sulfide system

A check on the data reported in the literature for the methane-hydrogen sulfide system at 1330 PSIA and 160°F. was made and good agreement was achieved as it is shown below:

$P = 1330$ PSIA $\quad T = 160°F.$

Mole fraction of CH_4:	Data of Reamer Sage and Lacey	This work
y	.270	.267
x	.085	.082

(b) The ternary system

The phase equilibrium at 160°F. has been described by the experimental determination of the dew point and bubble point loci at pressures of 1000 and 1600 PSIA by Lorenzo and at 1330 PSIA in this work. The experimental data at 1330 PSIA are reported in Table I in the appendix. The isobaric-isothermal phase diagram in Figure II illustrates the equilibrium at the pressure of 1330 PSIA which lies between the critical pressure of the carbon dioxide-hydrogen sulfide binary system (1220 PSIA) and of the methane-hydrogen sulfide binary system (1660 PSIA).

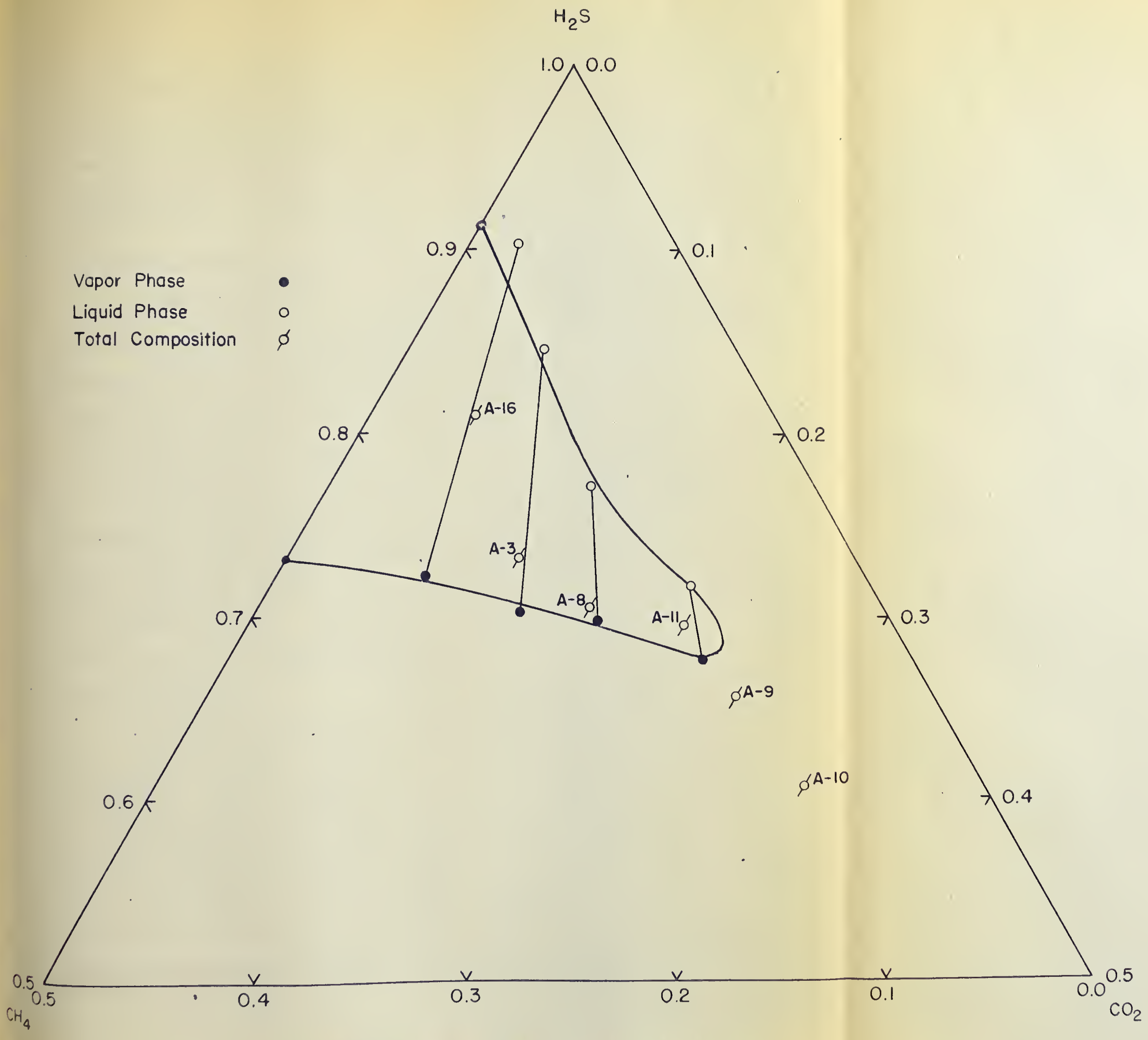


Figure -2. Experimental Phase Composition Diagram

T=160 °F P=1330 psia

Figure III illustrates the phase equilibrium of the system at 1300 PSIA and 160°F. as it was predicted by Lorenzo using his data at 1000 PSIA and 1600 PSIA as well as published data on the binary mixtures.

(2) Equilibrium ratios

Experimental equilibrium ratios for each of the three components were calculated at regular values of the parameter C up to 0.6 where the two phase loop eventually terminates. Table II in the appendix represents the experimental equilibrium ratios.

A substantial difference between the experimental K values for the three components at the pressure of 1330 PSIA and the K values, picked from the pressure vs K plots in Lorenzo's work is noted. Theoretical K values were also calculated employing equation (2) for each of the three components.

For the determination of the vapor pressure of methane and carbon dioxide, both being over their critical temperature at 160°F., an extrapolation of their vapor pressure vs temperature plots had to be made. The resulting vapor pressures were: methane: 9300 PSIA and carbon dioxide: 2350 PSIA. The hydrogen sulfide being below its critical temperature at 160°F., exhibits a vapor pressure of 779 PSIA.

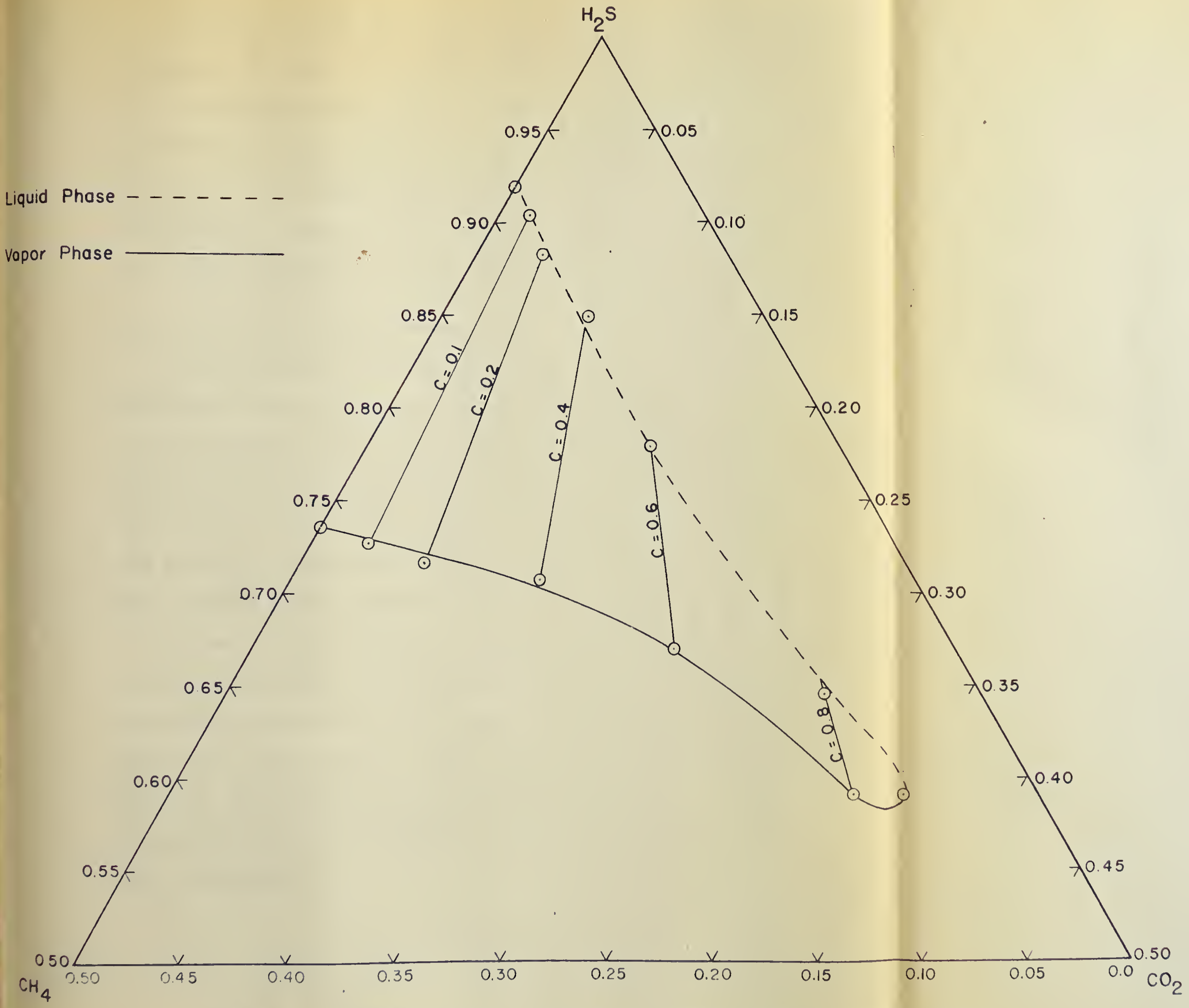


FIG. 3 PREDICTED MOLAR COMPOSITION DIAGRAM

T = 160 °F. P = 1300 lbs/in.^{2} abs.

Pressure-volume data were available for the pure components methane and carbon dioxide in the literature (15) and (4) respectively. Values of theoretical K for hydrogen sulfide at 160°F. were obtained from generalized fugacity charts (19) rather than by extrapolation. Theoretical K values at regular C values calculated as above are listed in Table III in the appendix.

(3) Activity coefficients ratios

The calculated theoretical K values were used to determine the activity coefficient ratios of the components in the system at 160°F. and pressure of 1330 PSIA which is indicative of the deviation of the liquid and vapor phases from the ideal behavior. Table III in the appendix shows the values of the calculated activity coefficient ratios of the components at regular C values.

Values of the activity coefficient ratios of less than unity indicate that the component actually exists in higher concentration in the liquid phase and lower concentration in the vapor phase than the ideal coefficient ratios predict. Activity coefficient ratios greater than unity indicate concentration of the component in vapor phase greater than the theoretical.

E. CONCLUSIONS

In an effort to discuss the accuracy of the obtained results, one should mention several factors that played a significant role in their achievement.

1. Temperature control at the temperature of 160°F. was a difficult matter because of the nature of the bath and the difference intemperature with the surroundings. A temperature gradient of 1°F. was always apparent between the top and bottom parts of the cell.

2. Pressure control was rather simple with an accuracy of ±2 PSIA for the high pressure range.

3. Volume measurements should be considered of an accuracy of better than ±0.5%. However, an uncertainty in the overall system composition remains because of several traps of gases in the way from the measuring cell to the equilibrium cell.

4. A serious cause of mistakes is due to the difficulty in separating the phases at equilibrium. Condensation due to throttling during the withdrawal of the gas phase and sudden pressure reduction destroying the achieved equilibrium necessitated repeats for several runs.

5. The analytical method could reproduce methane concentrations (Orsat apparatus) of better than ±1.0%. The hydrogen sulfide titration, using the Tutweiler burette, gave an overall ±1.0% error, achieved only by duplicating samples.

Although an overall error of ±1% in the phase composition could cause a substantial uncertainty in K values, and particularly for components in very small concentrations in the phases, the obtained results give a very good outline of the phase composition for the ternary mixture.

PART II. VOLUMETRIC BEHAVIOR OF THE METHANE-CARBON DIOXIDE-HYDROGEN SULFIDE SYSTEM IN THE VAPOR PHASE REGION AT TEMPERATURES OF 160°, 100° and 40°F. AND PRESSURES UP TO 3000 PSIA.

F. INTRODUCTION - THEORY

The primary purpose of the experimental program carried out in this main part of the thesis was an investigation into the volumetric behavior of the methane-carbon dioxide-hydrogen sulfide system in the single (vapor) phase region. Thus, the compressibility factor of a number of mixtures representative of the single phase (vapor) region was measured at temperatures of 40, 100 and 160°F. and at pressures up to 3000 PSIA.

The compressibility factors of several mixtures of varied composition of the carbon dioxide-hydrogen sulfide binary system at 160°F. were also investigated.

Finally, an attempt was made to compare the obtained compressibility factors with the ones calculated by using various correlation methods for mixtures such as the Amagat's, Gilliland's and Kay's methods.

The basic equation expressing the PVT behavior of gases is the ideal law:

$$P\bar{V} = \frac{RT}{M} \quad \text{(eq.8)}$$

Thus as expressed by equation (8), the volume of a unit weight of an ideal gas at any equilibrium temperature and pressure can be evaluated solely from a knowledge of the molecular weight of the gas.

In practice, it has been found that no gas obeys this simple law over all pressures and temperatures.

The molecules of real (as distinct from ideal) gases occupy a certain definite volume that may or may not be negligible in comparison with the total volume occupied by the gas; furthermore, they possess fields of force resulting in attractive forces between them. Both these conditions lead to the fact that as the molecules of a gas approach one another (or as the gas becomes denser) the gas departs more and more from the ideal state.

In a few cases, unusually large deviations from the ideal-gas laws occur even at relatively low pressures. These are thought to be due to chemical changes resulting in association or dissociation of molecules. Hydrocarbons, in particular, deviate widely from the ideal gas law at the elevated pressures and temperatures of petroleum reservoirs.

In order to express a more exact relationship between the variables P, V and T a correction factor must be introduced into equation (8).

Either of two methods is normally used: The first method introduces a multiplying factor into the right side of the equation (8) and the second method makes use of an addition factor. The multiplying factor goes by several names; three of the most common are "compressibility" factor, "deviation"

factor and "super-expansibility" factor. The compressibility factor and deviation factor are synonymous, and the super-expansibility factor is the reciprocal of these two factors. The addition factor α is termed the "residual volume". Both methods are accurate to the same degree, but the first is easier to use and therefore the most popular. The "residual volume" correlation, however, is of a wide use in the determination of other thermodynamic properties of mixtures employing PVT data.

The compressibility factors of different gaseous components vary over wide ranges of elevated pressures.

During the 1860's many papers appeared in the literature concerning PVT behavior of individual gases. J. D. van der Waals (7) in 1873 developed the theorem of corresponding states on which the modern correlation of compressibility factors is based. The theorem proposes that all gases will exhibit the same behavior when viewed in terms of reduced pressure, reduced volume, and reduced temperature. The term "reduced" means that each variable is expressed as a ratio of the critical value. Thus, all variables are reduced to a common datum, the value of the critical. The reduced conditions of volume, temperature and pressure are expressed as:

$$V_R = \frac{V}{V_C} \; , \; T_r = \frac{T}{T_C} \; , \; P_r = \frac{P}{P_C}$$

The theorem of corresponding states when applied to gases having similar chemical structure (as the paraffin hydrocarbons), offers a correlation method with satisfactory accuracy for engineering work. However, the theorem of corresponding states is not perfect leading to a greater deviation when dealing with gases of different molecular structure.

The importance of either Z or α lies in the ability to correlate relatively accurately the values for different gases by use of the reduced conditions and the consequent elimination of use of complicated equations of state involving a multitude of constants or higher degree equations, with virial coefficients, such as found in the theoretical van der Waals and Beattie-Bridgmann or the empirical Maron and Turnbull or Benedict-Webb-Rubin equations.

Compressibility of Mixtures:

Although a relatively accurate method for predicting compressibility factors of the single components is provided through the use of reduced conditions - compressibility charts, determination of the correct values of compressibility factors for mixtures is somewhat difficult.

Two general methods of dealing with gaseous mixtures have been proposed. The first assumes additivity direct or

modified of certain physical properties of the mixture in terms of those of the components; the second averages the constants of an equation of state applicable to the pure components. The familiar illustrations of the first method are Dalton's (11) and Amagat's (11) laws. It has been generally assumed that Amagat's law reproduces the experimental data better than Dalton's.

The attempt to average constants in an equation of state goes back at least to van der Waals. The method has been most successfully developed by Beattie (8), but is complicated for engineering work and limited by lack of the necessary constants for most substances.

Several other methods have been proposed for the treatment of problems involving mixtures but any or all may break down in the critical region.

A more extensive use of two of them, namely Kay's rule and Gilliland's method is made for the treatment of a variety of mixtures (9, 10).

Amagat's method, and also Kay's and Gilliland's method, will be discussed in the correlation of the experimental data.

G. EXPERIMENTAL TECHNIQUE

The experimental procedure consisted of confining a known mass of sample, of definite composition, over mercury in the variable volume equilibrium cell. The sample was thermostated, and a known pressure was applied. After equilibrium was attained, the volume was determined by measuring the length of the column of sample by use of the cathetometer; this length was related to the volume by a prior calibration of the cell.

Thus, each complete run was separated into several distinct portions which included makeup of the desired system, achievement of equilibrium conditions within the system and the measurement of the variables, i.e., temperature, pressure and volume:

1. Addition of Hydrogen Sulfide:

With the equilibrium cell temperature at the desired level the run started with the introduction of hydrogen sulfide into it, after a previous evacuation of the lines leading to the equilibrium cell, and consequent purging by the hydrogen sulfide. After a brief time interval to allow the hydrogen sulfide to reach thermal equilibrium, its temperature, pressure and volume were recorded and thus a calculation of the number of moles of hydrogen sulfide added was possible.

2. Carbon dioxide and methane had to be determined individually in the measuring cell. Since the number of moles of carbon dioxide and methane was fixed by the knowledge of the desired overall system composition and the number of moles of hydrogen sulfide already in the equilibrium cell, the volumes of each component needed in the measuring cell could be predetermined for the pressure at which they were to be added and temperature of the measuring cell. The order in which methane and carbon dioxide were measured and introduced into the equilibrium cell was not fixed; the procedure, however, was the same for each component. After the desired amount of each of the single components had been added and their number of moles had been calculated, the single component was injected into the equilibrium cell by mercury displacement from the measuring cell.

3. The temperature in the equilibrium cell was measured with 3 one-junction copper-constantan thermocouples and a potentiometer reading to 2.5 microvolts. A one-junction similar thermocouple was employed for the measuring cell.

4. Pressures were determined with a 0-3000 PSIA Heise gauge for the higher pressure and with both the above mentioned gauge and a 0-1000 PSIA for the lower pressure range. The gauges were calibrated against a dead-weight piston gauge and proper calibration curves were employed.

Suitable corrections were made for the various hydrostatic heads existing between the sample and the gauges.

5. A cathetometer was used to measure the sample volume and to determine the hydrostatic heads which contributed to the measured pressure. The reproducibility of the length measurements was about ± .05 mm., corresponding to a precision in volume measurements of about .01% for the largest volumes observed, and about 0.1% for the smallest ones. However, the encountered error should be considered as being greater.

The measurements of temperature, total volume and equilibrium pressure were obtained upon both increase and decrease in the total volume of the system. The agreement of the values obtained by these two approaches to a given state indicated that the attainment of a steady state was satisfactory.

The study was carried out in the same apparatus that had been used for the phase equilibrium measurements in the first part of this work and no modifications of it were attempted. However, a more precise cathetometer was used for the measurement of volume and refrigeration coils replaced the heating coils for the study at 40°F.

H. EXPERIMENTAL RESULTS

1. The Binary System at 160°F.

The experimental program included the investigation into the volumetric behavior of three binary mixtures of carbon dioxide and hydrogen sulfide at the temparature of 160°F. Table (IV) in the appendix and Figure (4) represent the results obtained.

Since the maximum pressure during the investigation did not exceed 1800 PSIA the compressibility factor experimental line was arbitrarily extended up to 3000 PSIA (dash line).

The investigation of the ternary system included the study of the volumetric behavior of several mixtures at the three mentioned temperatures of 160, 100 and 40°F. and pressure up to 3000 PSIA. An attempt was made to keep the methane to carbon dioxide mole ratio at 4:1 and vary the hydrogen sulfide content; however, this rule has not been followed closely in the preparation of the ternary mixtures at the temperature of 40°F. since the single phase (vapor) region is limited allowing the preparation of only two mixtures similar to those prepared at the temperatures of 100° and 160°F.

2. The Ternary Mixture at 160°F.

At the temperature of 160°F. the following five mixtures were investigated:

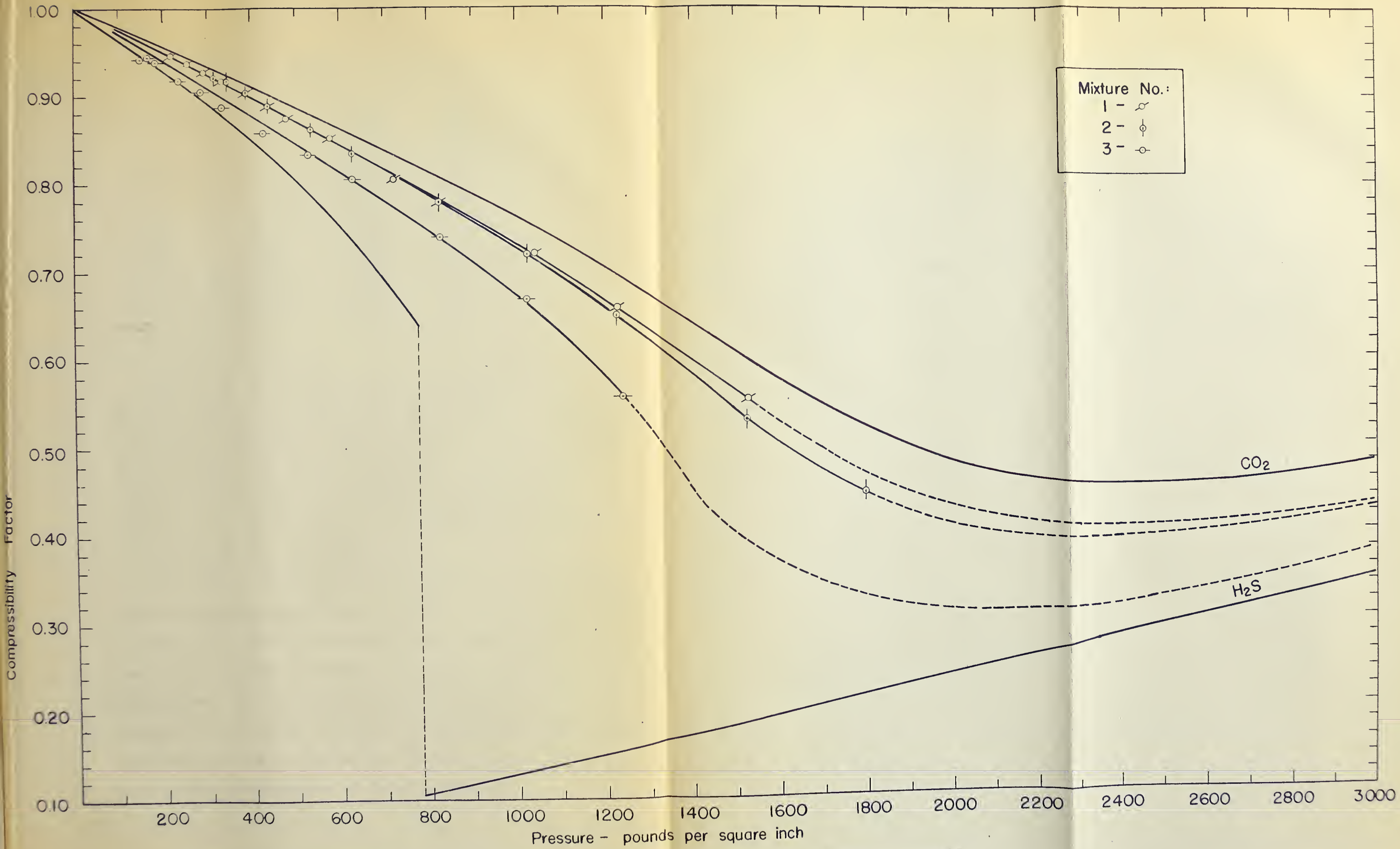


Figure - 4. Compressibility of the Carbon Dioxide - Hydrogen Sulphide Binary Mixtures at 160 °F.

Table

Mixture No.	y_{H_2S}	y_{CO_2}	y_{CH_4}
I	.0392	.1814	.7794
Ia	.0426	.1816	.7756
II	.1252	.1751	.6997
IIa	.1118	.1728	.7154
III	.2331	.1538	.6131
V	.0857	.3660	.5483
VI	.5256	.1044	.3700

Since for mixtures No. I and II the total number of moles added to the equilibrium cell exerted a pressure of well over 700 PSIA to start with, i.e., with the sample occupying the total volume of the cell, two additional mixtures No. Ia and IIa, corresponding respectively to mixtures No. I and II, had to be prepared for the range of pressure between 0 and 700 PSIA.

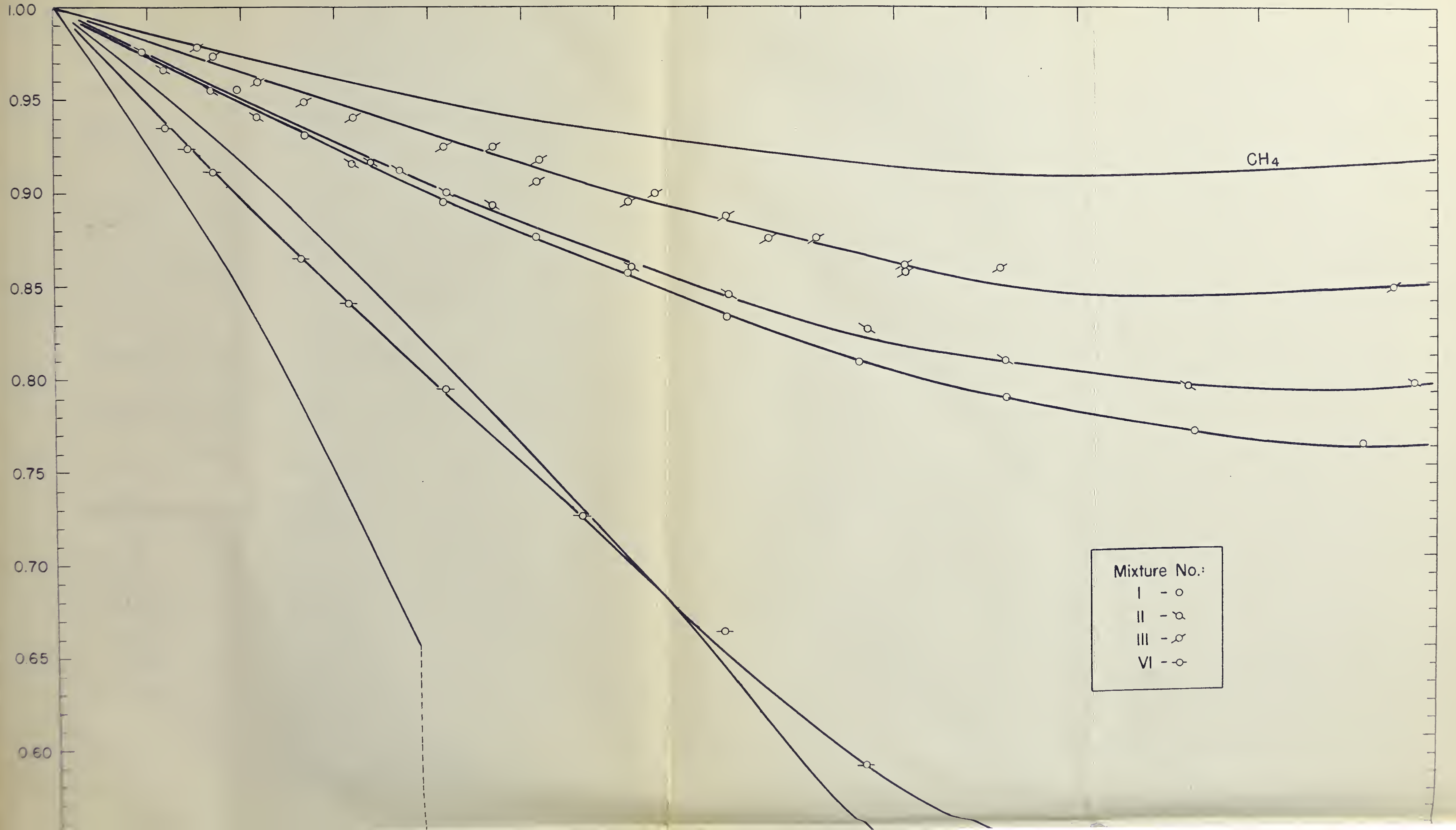
To cover the entire range of pressures in the measurements of the compressibility of gases, a conventional method is employed so that the same mixture is kept in use for both high and low pressure ranges. It consists of adding a relatively great number of moles into the equilibrium cell and after measurements have been obtained for the high pressure range, releasing part of the sample so that the remaining gas would permit measurements at lower pressures.

For the determination of the number of moles of the remaining gas, a compressibility factor taken from the data obtained at the high pressure region must be employed, and thus, an error introduced during the investigation at high pressures would be accumulated in the measurements at the low pressure region. This reason, and the fact that for a length of time an uncertainty had arisen regarding the validity of the volume calibration curves in use, imposed the earlier mentioned procedure, i.e., make up of two identical mixtures, one for the high pressure region and the other for the low pressures.

Table (V) in the appendix, and Figure (5) represent the experimental compressibility factors for the above mentioned mixtures. Mixture V for which the methane to carbon dioxide mole ratio is other than the stated 4:1, consists an intermediate path in the preparation of mixture Ia from mixture IIa. The maximum investigation pressure, for this mixture, did not exceed 1000 PSIA.

3. The Ternary Mixture at 100°F.

Establishing the new temperature of 100°F. in the equilibrium cell, data were obtained for five of the above mentioned mixtures, namely, I, Ia, II, IIa and III. Mixture IV (yH_2S : .1989, yCO_2 : .2781; y_{CH_4} : .5230) was also


1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
CH4
Mixture No.:
I - ○
II - ○
III - ○
VI - ○

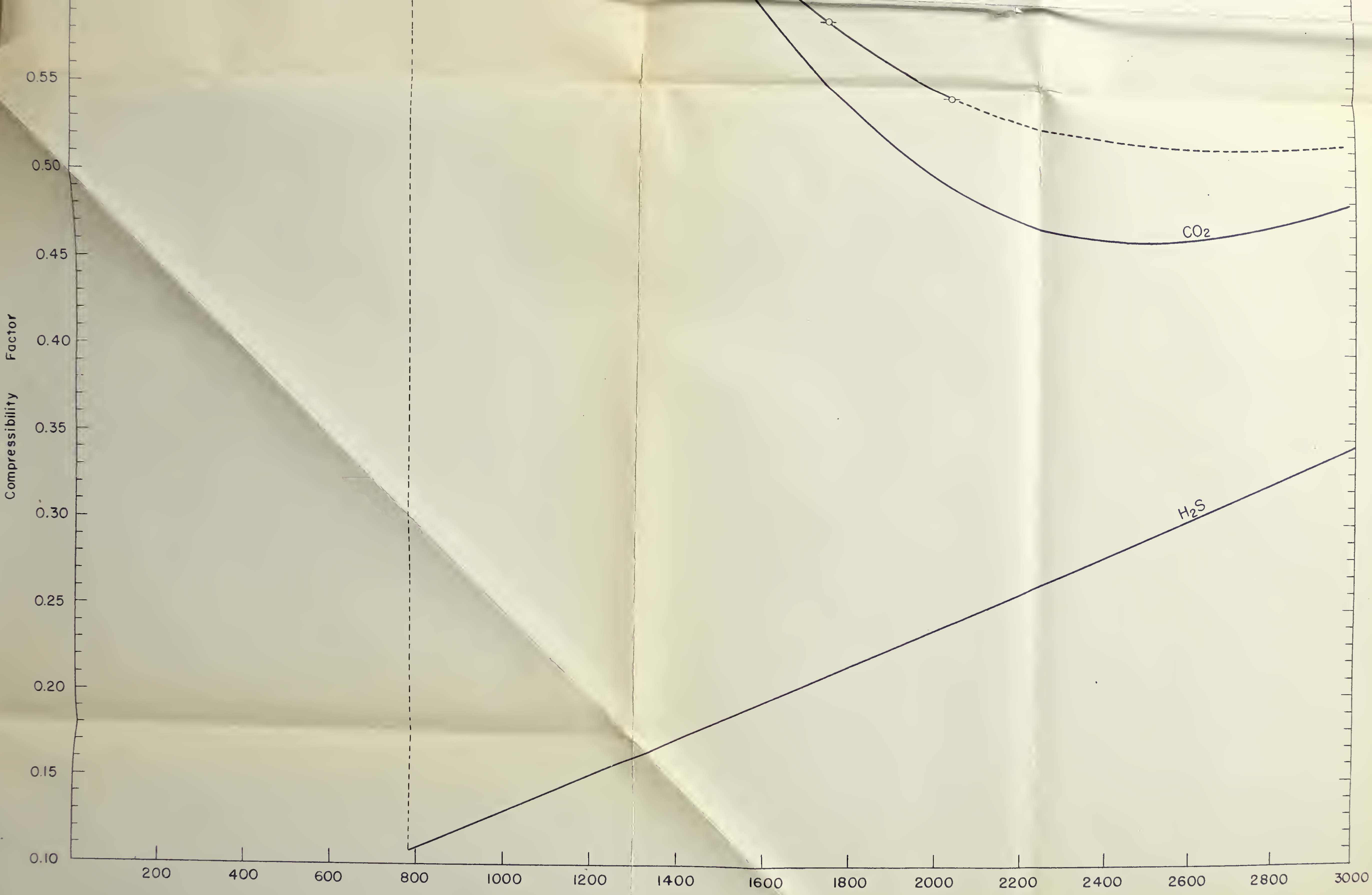


Figure – 5. Compressibility Factor Correlation of the Experimental Data for the Ternary Systems at 160 °F.

investigated, consisting a path in the preparation of Mixture II from mixture III.

Table (VI) in the appendix and figure (6) represent the experimental compressibility factors obtained at this temperature.

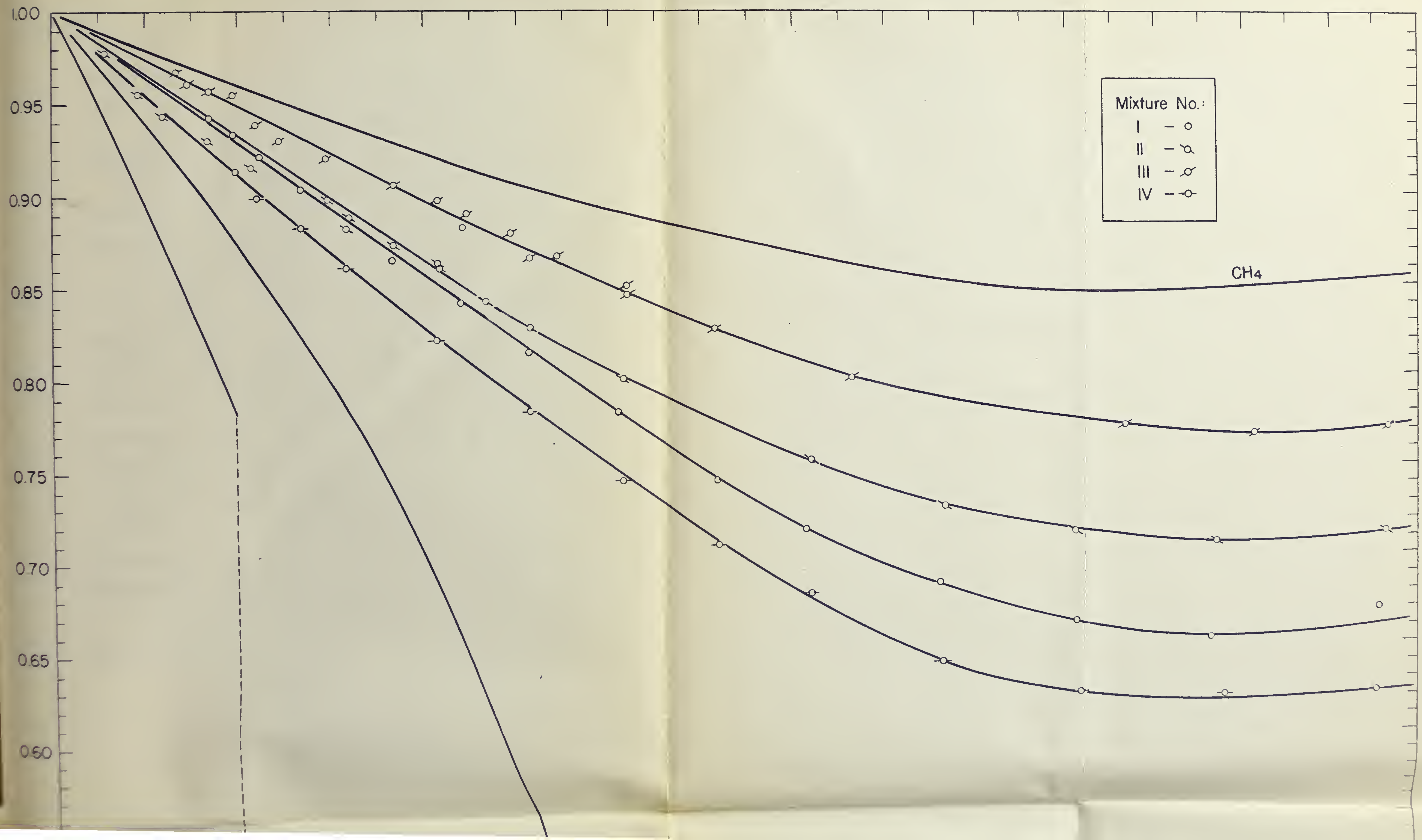
4. The Ternary Mixture at 40°F.

At this temperature, where the isobaric loops extend considerably towards rich in carbon dioxide and methane, and poor in hydrogen sulfide mixtures, only two mixtures, namely, XI and XIII were studied having their methane to carbon dioxide mole ratio 4:1. However, three other mixtures were investigated in an attempt to cover the vapor phase region considerably.

The following table indicates the composition of the mixtures investigated at 40°F.

Table

Mixture No.	Y_{H_2S}	Y_{CO_2}	Y_{CH_4}
XI	.2440	.1575	.5985
XII	.2095	.2760	.5145
XIII	.1338	.1762	.6900
XV	.1475	.2965	.5560
XVI	.1178	.2365	.6457


1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
Mixture No.:
I – ○
II – ○
III – ○
IV – -○-
CH4

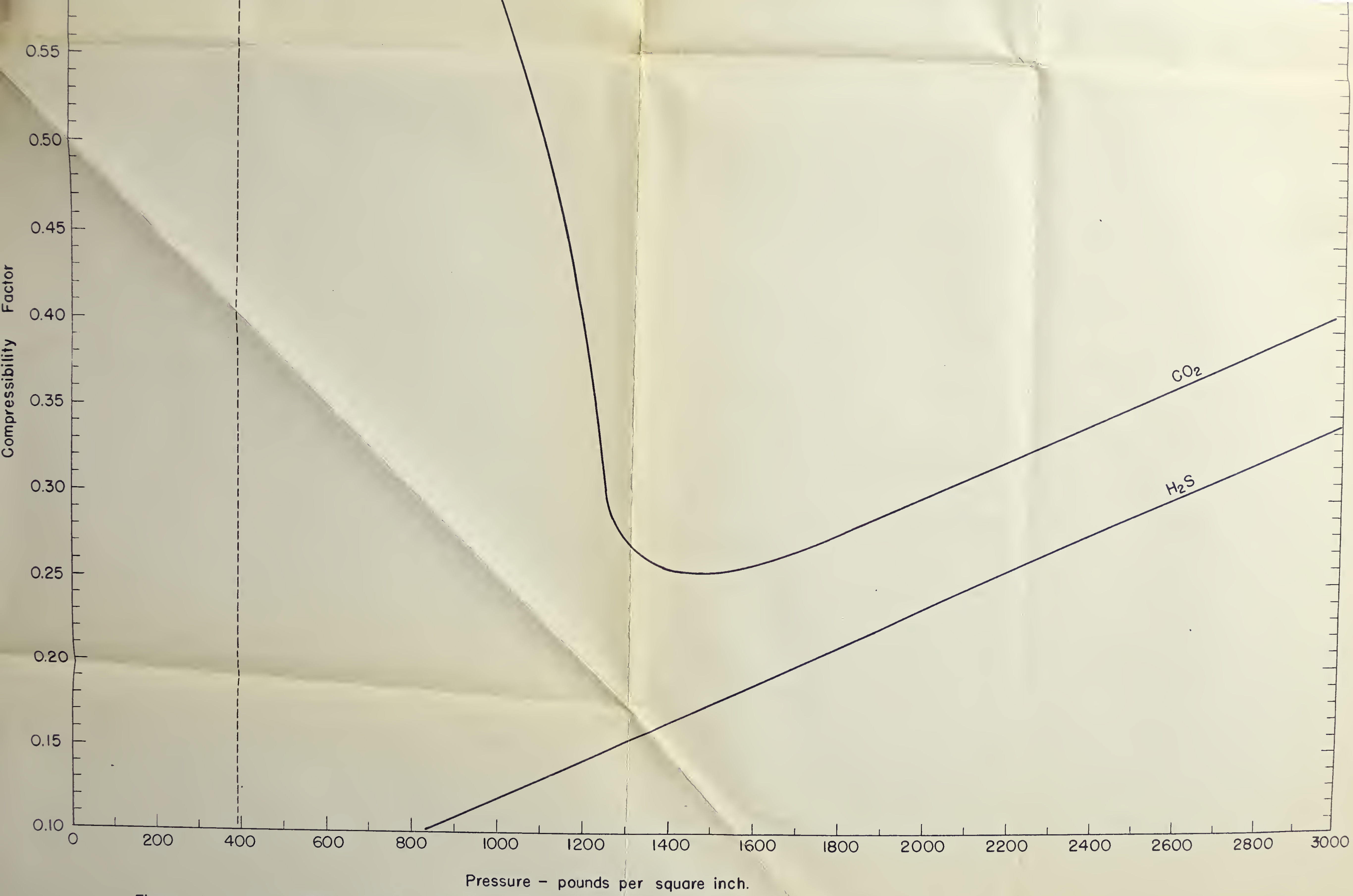


Figure – 6. Compressibility Factor Correlation of the Experimental Data for the Ternary Systems at 100 °F.

Mixtures at 40°F. were studied after the investigation at 160°F. and 100°F. was entirely completed, so that new mixtures had to be prepared.

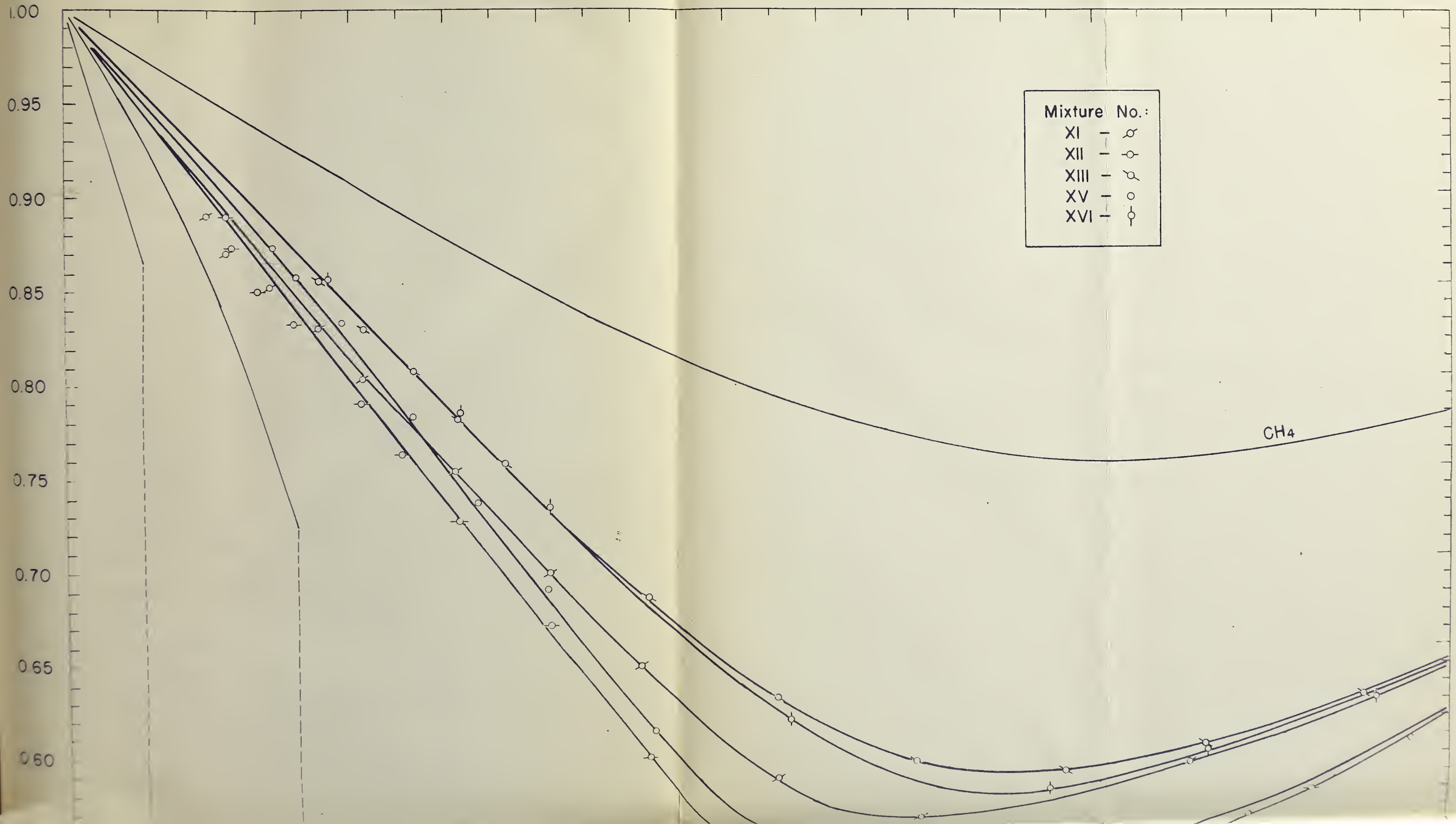
Table (VII) in the appendix and Figure (7) represent the experimental compressibility factors obtained at the temperature of 40°F.

Discussion

A check on the consistency of the results obtained was done by employing the single components, methane, carbon dioxide and hydrogen sulfide.

An amount of a single component was introduced into either the equilibrium cell or the measuring cell and after the desired temperature was established, the number of moles of the gas was calculated employing a compressibility factor taken from the literature. Then the pressure was increased and the new volume of the gas in the cell was recorded. The procedure was followed until the maximum desired pressure was reached. Then, employing the as above found number of moles, the compressibility of the pure gas was calculated. The obtained compressibility factors were then compared to those reported in the literature.

For a variety of temperatures, in both the equilibrium and the measuring cell, and a number of approximately 30


1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
Mixture No.:
XI –
XII –
XIII –
XV –
XVI –
CH4

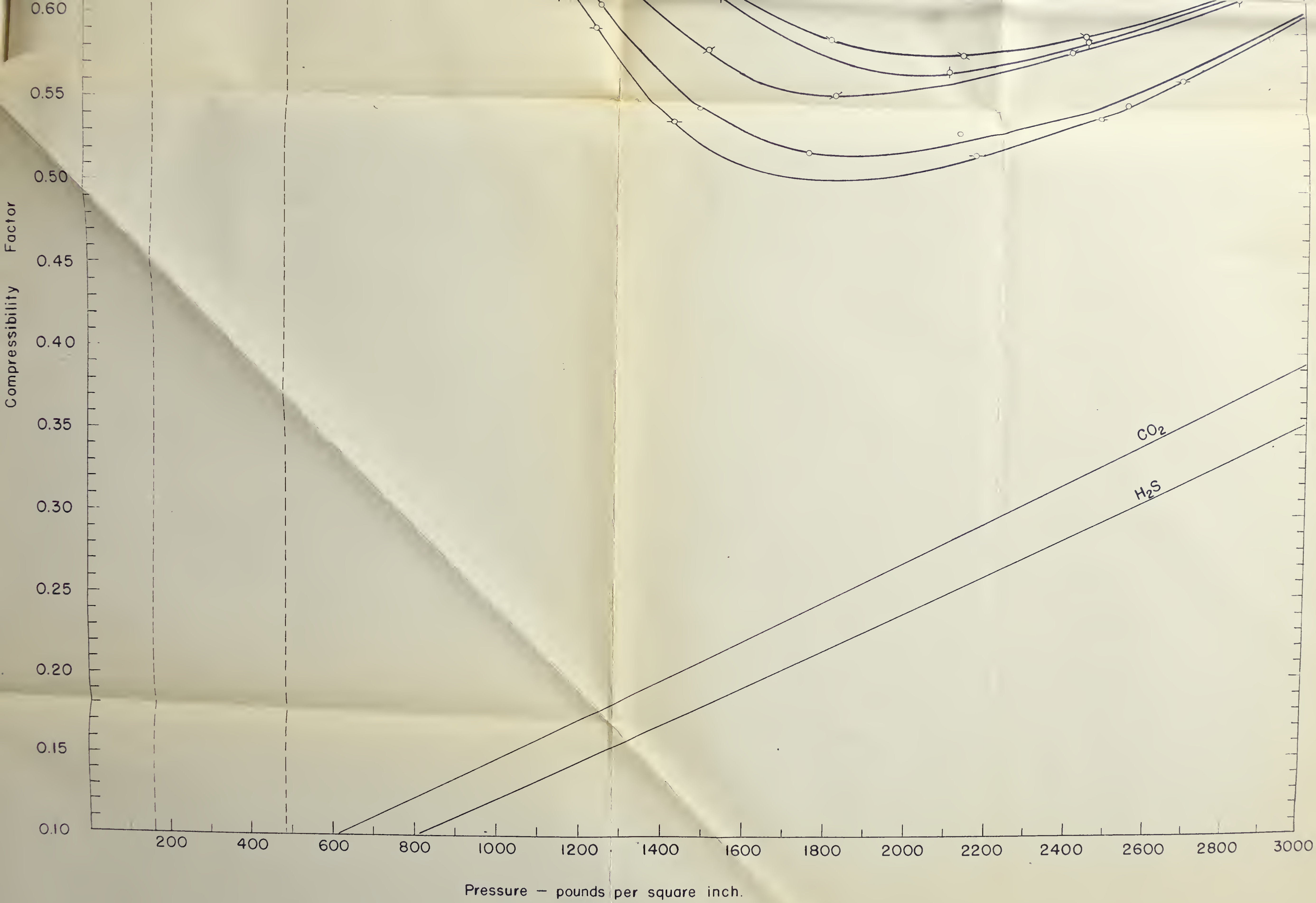


Figure-7. Compressibility Factor Correlation of the Experimental Data for the Ternary Systems at 40 °F.

single component runs and pressures up to 2500 PSIA, the error encountered was less than ± 2.5%.

Another check was made by making up an approximately 50-50 methane to carbon dioxide binary system for which compressibility data have been published (13). The agreement in the compressibility factors was better than ±1.0% and for pressures up to 3000 PSIA.

II. Correlation of the Experimental Data

1. Amagat's Method and its Application to the Binary and Ternary Systems.

Amagat's law leads to a simple relation:

$Zm = Z_A Y_A + Z_B Y_B + Z_C Y_C + \ldots$ where Zm is the mean compressibility factor of the mixture, Z_A, Z_B . . . are compressibility factors of the pure components at the total pressure and temperature of the system and Y_A, Y_B . . . are mole fractions of components A,B . . . A disadvantage of the method is that when the conditions assume the liquid phase for one or more of the components in the mixture, additivity of volumes cannot be assumed anymore. Tables (VIII, IX, X) in the appendix and Figures (8,9,10) show a comparison of the experimentally obtained compressibility factors of several ternary mixtures, to those obtained by applying the Amagat method of prediction to the same mixtures at the same conditions. Compressibility factors for the pure components, employed in these calculations, were taken from (13,14) and (15,16); the reported experimental compressibility factors of the mixtures, in comparison, have been taken from smoothed experimental curves.

Figure (8) represents a typical plot of percent deviation of values of compressibility factors calculated by Amagat's method (dash lines) from those obtained experimentally (solid line). The four (dash) lines represent mixtures No. I, II, III and VI at the temperature of 160°F.

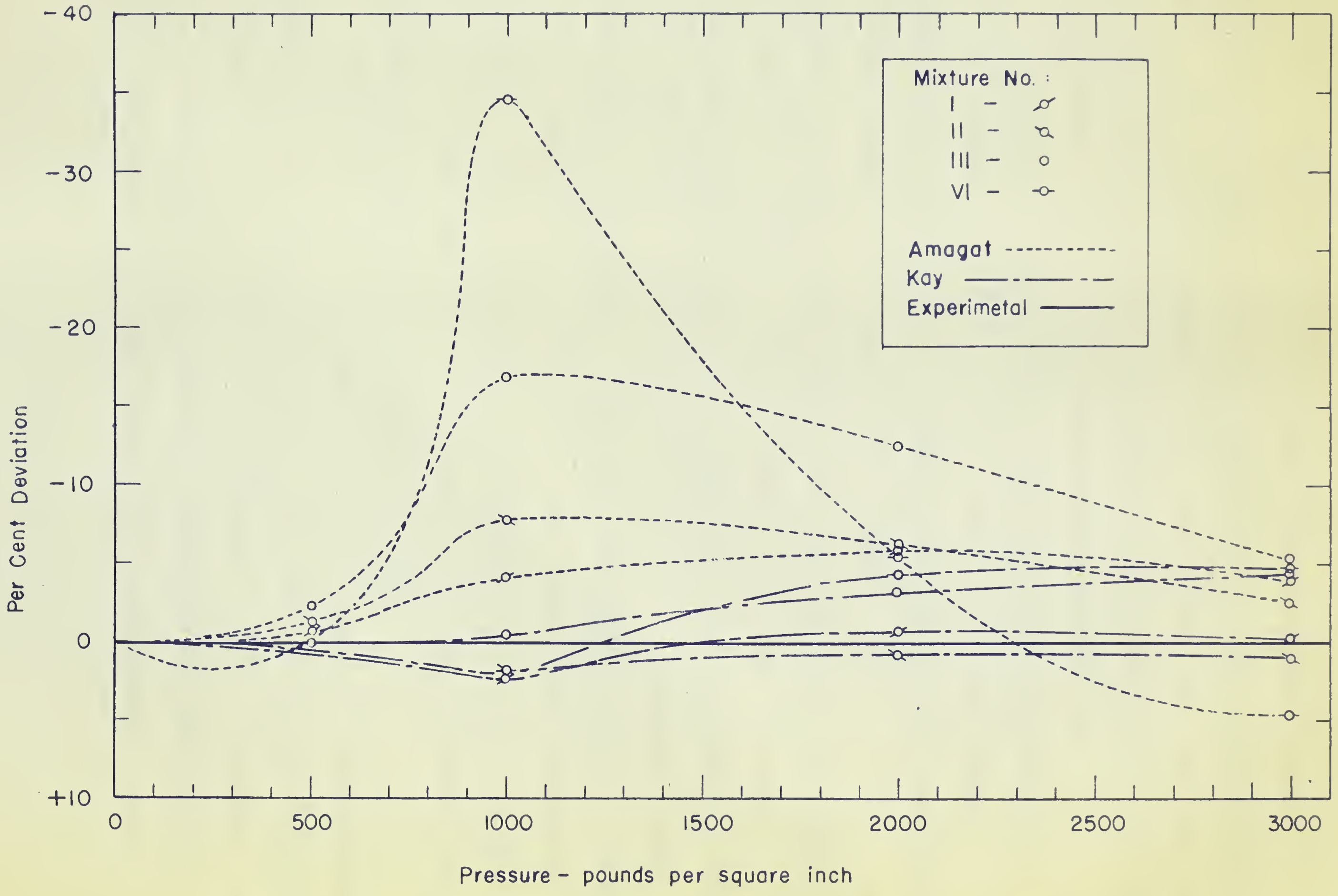


Figure - 8. Experimental And Calculated Compressibility of the Ternary Mixtures at 160 °F.

A maximum discrepancy from the experimental values is apparent in this figure for pressures in the neighborhood of 1000 PSIA. It is also apparent that the greater the hydrogen sulfide content in the mixture, the greater the discrepancy from the experimental value of the compressibility factors.

Looking at Table (VIII) we see that the contribution by the hydrogen sulfide to the value of the calculated compressibility factor by Amagat's method, at the mentioned pressure region and temperature of 160°F. and for all of the mixtures is negligible compared to that of the carbon dioxide and methane content. This is due to the fact that the conditions impose the liquid phase for the hydrogen sulfide, resulting thus, in non-applicability of the Amagat method, as it is stated previously. The same behavior is seen in Figure (9) representing mixtures I, II, III at the temperature of 100°F. Here the maximum discrepancy occurs at a pressure in the neighborhood of 500 PSIA since the equilibrium pressure of hydrogen sulfide is now only 394 PSIA.

Comparing the apparent discrepancy from the experimental values of each one of mixtures I, II, III at the two temperatures and pressures up to 2000 PSIA (Figures 8, 9) we see an increase as the temperature decreases. For pressures of 2000 PSIA to 3000 PSIA the discrepancy follows the temperature variation.

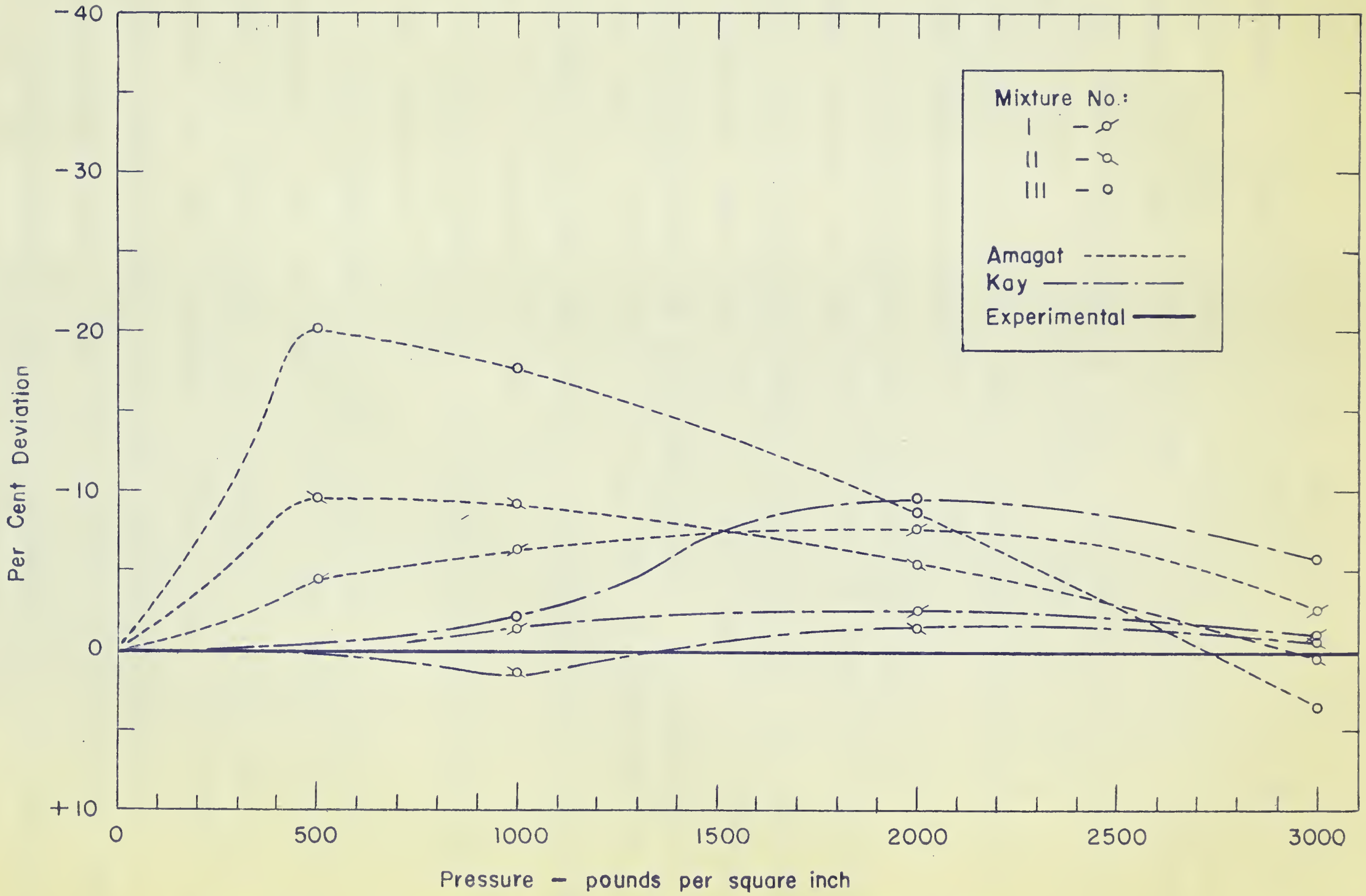


Figure - 9. Experimental And Calculated Compressibility of the Ternary Systems at 100 °F.

In Figure (10), at the temperature of 40°F., the maximum discrepancy occurs over the same pressure region as for the mixtures at 100°F. However, for the very low pressure region - (pressures between 0 and 500 PSIA - the discrepancy is greater at the lower temperature of 40°F. The above conclusions can be drawn by looking at the discrepancy curves, in Figure (10), of mixtures XI and XIII, which are similar to mixtures III and II at the temperature of 100°F. and 160°F.

It is worth noticing that mixture No. VI of the highest hydrogen sulfide concentration at the temperature of 160°F. and for pressures between 2000 and 2600 PSIA exhibits a discrepancy much lower than any of the poorer in hydrogen sulfide mixtures at the same temperature. For pressures between 2600 and 3000 PSIA and also 1400 to 2000 PSIA its discrepancy is lower than that of mixture No. III, reversing sign at the pressure of 2300 PSIA.

A similar behavior is noticeable for mixture No. III at the temperature of 100°F.

At the temperature of 40°F. where for both hydrogen sulfide and carbon dioxide and for a wide pressure range, conditions impose the liquid phase, the discrepancy is much greater following an order of methane concentration. The higher the methane concentrations, the lower the discrepancy from the experimental values. Here also, and for pressures over 2000 PSIA, the discrepancy diminishes substantially with the deviation curves on either side of the experimental datum.

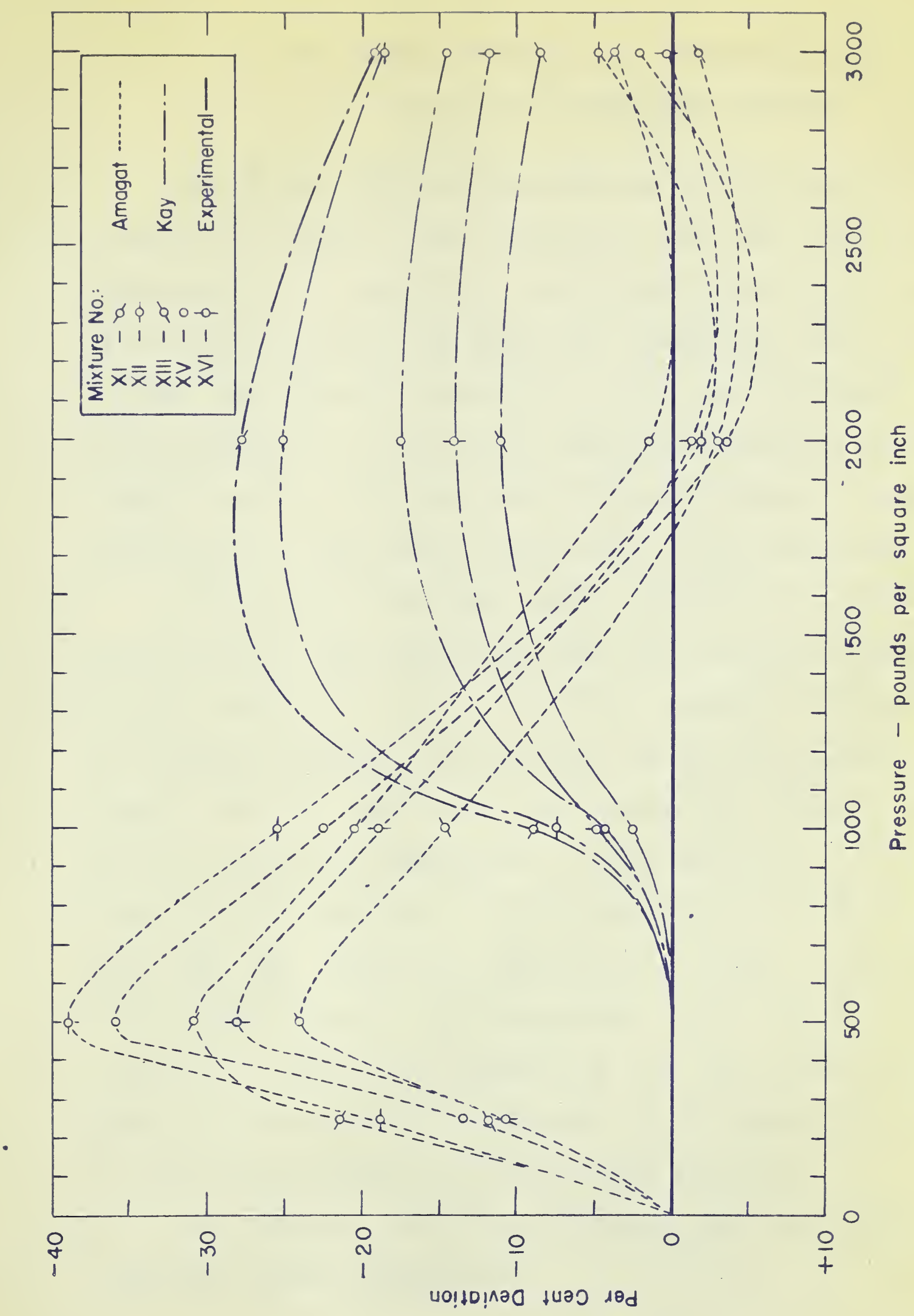


Figure - 10. Experimental And Calculated Compressibility of the Ternary Systems at 40 °F.

2. Gilliland's Method and its Application to the Binary and Ternary Systems.

One of the classical approaches to the study of the behavior of gases is the assumption that the total volume occupied by the gas may be considered as made up of the effective volume of the molecules themselves and of the free volume available for molecular motion, and similarly that the total pressure is the sum of the actual pressure externally exerted upon the gas and the so-called internal pressure, equivalent to the mutual attraction of the molecules.

Also, one of the most useful correlations of the PVT properties of pure gases has been the graphical representation of the isometrics, i.e., a graph of pressure vs temperature at constant volume. In the range above the critical temperature the isometrics are essentially straight lines for a large number of substances. Lewis and Luke (17) have expressed the equation of the isometric as $P = \phi_1 T - \phi_2$ with ϕ_1, ϕ_2 being only functions of volume if the isometrics are straight lines. The reciprocal of the slope of the isometric ($1/\phi_1$) is a measure of the free volume and the negative intercept of the tangent to the isometric (ϕ_2) is generally defined as the internal pressure.

For mixtures, Gilliland presumes that the above equation can be written as:

$$P_{mix} = (\phi_1)_{mix} T - (\phi_2)_{mix} \quad \text{where}$$
$$(\phi_1)_m = y_A (\phi_1)_A + y_B (\phi_1)_B + . . \text{ and}$$
$$(\phi_2)_m = (y_A \sqrt{(\phi_2)_A} + y_B \sqrt{(\phi_2)_B} + . . .)^2$$

For binary systems the equation could be written as:

$$\text{(eq.9)} \quad P_{mix} = y_A P_A + y_B P_B + y_A y_B (\sqrt{(\phi_2)_A} - \sqrt{(\phi_2)_B})^2$$

The values of P_A, P_B are pressures exerted by the pure components alone under the existing temperature and molal volume. Values of $(\phi_2)_A$, $(\phi_2)_B$ are calculated from a plot of V_r vs $(\phi_2)_r$ for each component. Equation (9) becomes more complicated when more than two components are present.

The method is a very tedious one and hence of little use at present. An attempt was made to compare the experimentally obtained data for the hydrogen sulfide-carbon dioxide system to values calculated by this method. The agreement between the calculated compressibility for the mixture and the experimental was comparable to that obtained by using Kay's method for the ternary system as it will be shown later. An outline of the method employed is as follows:

From pressure vs compressibility factor tables for the pure components carbon dioxide (4) and hydrogen sulfide (14) the isobaric, i.e., temperature vs molal volumes at constant pressures, lines are plotted. Pairs of values of temperature and pressure for equal volumes are picked on the isobarics which are then plotted on a temperature vs pressure graph

forming the so-called isometrics. The isometrics for carbon dioxide are very well straight lines, the isometrics for hydrogen sulfide however are lines with a slight curvature. Extrapolation of the carbon dioxide straight isometrics until they cut the pressure ordinate then follows. Extrapolating the straight part of the hydrogen sulfide isometrics, we are also able to obtain the intercepts with the pressure ordinate. Since the negative values of this intercept represent value ϕ_2 in the isometrics we then tabulate V (isometrics) vs ϕ_2 for carbon dioxide and for hydrogen sulfide. Dividing V by the critical volume of each of the components and ϕ_2 by the critical pressure of each of the components we finally evaluate V_r and $(\phi_2)_r$ for each of the components. The V_r vs $(\phi_2)_r$ correlation is shown for hydrogen sulfide and carbon dioxide in Figure (11) in the appendix. The method then follows a trial and error procedure which is thoroughly developed in the appendix (page 84) and for the compressibility factor of carbon dioxide-hydrogen sulfide mixture No. 2 at 1000 PSIA and 160°F.

3. Kay's Method and its Application to the Binary and Ternary Systems.

As it was stated previously, the modern form of the theorem of corresponding states covers nearly all pure compounds so that the calculation of their compressibility at any condition is not a difficult matter anymore. If the data on complex mixtures are plotted in a similar manner by employing the actual critical pressure and temperature of the mixture for the calculation of the reduced properties, the resulting curves deviate considerably from those of pure compounds, particularly in the critical region.

W. B. Kay stated that this is due to the improper selection of the critical point.

Obviously, if the data in the superheated region are to be compared with those for a pure compound by the theorem of corresponding states, the logical point for calculating the reduced quantities is not the actual critical point but a point which is the critical point of the pure compound whose PVT relations in the superheated region are identical with those for the mixture. If, then, the pressure and temperature of this point are known, the PVT relations in the superheated region can be calculated exactly as they would be for a pure compound, regardless of the boiling range of the mixture. This point may be called the "pseudocritical point" of the mixture since it is analogous to the critical point of a pure compound.

The difference between this point and the actual critical point is dependent on the width of the boiling range of the mixture. As the boiling range is diminished, the critical point approaches the pseudocritical and the two points coincide and are identical in the case of a pure compound.

Since the pseudocritical point of a mixture has no real existence, it cannot be measured. However, it may be estimated graphically from the PVT data on the mixture.

A thorough investigation on hydrocarbon mixtures made by W. B. Kay (9) yields the following simple relation for the pseudocritical pressure and temperature of the mixture:

$$(Tc)\ mix = Tc_A Y_A + Tc_B Y_B + \qquad (eq.10)$$

$$(Pc)\ mix = Pc_A Y_A + Pc_B Y_B + \qquad (eq.11)$$

where Tc_A, Tc_B . . . are critical temperatures of pure A, B . . . and Pc_A, Pc_B . . . are critical pressures of A, B . . .

This method has the advantage of using the same methods of solution of problems involving pure gases and vapors. Another inherent advantage of Kay's method is the ability to handle mixtures where the Amagat rule would find that the conditions imposed the liquid state on one or more components.

In the original communication of Kay (9), it is remarked that for mixtures whose constituents differ greatly in

molecular weight as well as chemical nature, values of the pseudocritical pressure and temperature, calculated as above (eq.10,11), are likely to be in error by an amount greater than that allowable in most engineering calculations.

Figures (8,9,10) and tables(XI,XII,XIII)in the appendix show the calculated compressibility factors for most of the studied ternary mixtures. In broken lines and in Figure (8) the discrepancy between calculated and experimental values for mixtures No. I, II, III, VI is shown at the temperature of 160°F.

In general, we see a better approximation achieved by using Kay's method over the entire range of pressure than Amagat's at this temperature. However, although the error is much more consistent and much lower, it exceeds the allowable for many engineering calculations proving the time-consuming experimental investigations absolutely necessary.

On Figure (9), representing mixtures No. I, II and III at the temperature of 100°F., we observe nearly the same behavior of Kay's method. However, an increasing discrepancy for mixture No. III (highest hydrogen sulfide concentration) is apparent at this temperature and for the range of higher pressures, i.e., over 1500 PSIA.

This phenomenon is more pronounced in Figure (10) representing ternary mixtures at the temperature of 40°F. At this temperature and pressure over 1000 PSIA the discrepancy

from the experimental values of the compressibility factors becomes much greater than that obtained using the Amagat's correlation method. With only one exception (mixture No. 1) the discrepancy increases as the methane content decreases or as the sum of hydrogen sulfide plus carbon dioxide increases.

At this temperature, and pressures over 1000 PSIA, since both hydrogen sulfide and carbon dioxide are in the liquid phase, the systems depart greatly from ideality.

This reason, and the fact that both acidic constituents of the ternary mixtures, i.e., carbon dioxide and hydrogen sulfide differ considerably in molecular weight and chemical structure from the main hydrocarbon component of the mixture, i.e., methane, may well explain the greater discrepancy observed.

4. Residual Volume Correlation

As was stated in a previous chapter, the compressibility factor, when plotted against reduced conditions, provides a very satisfactory correlation of PVT data. Vapor pressure volumes of pure compounds estimated from this type of plot are of sufficient accuracy for most engineering design calculations.

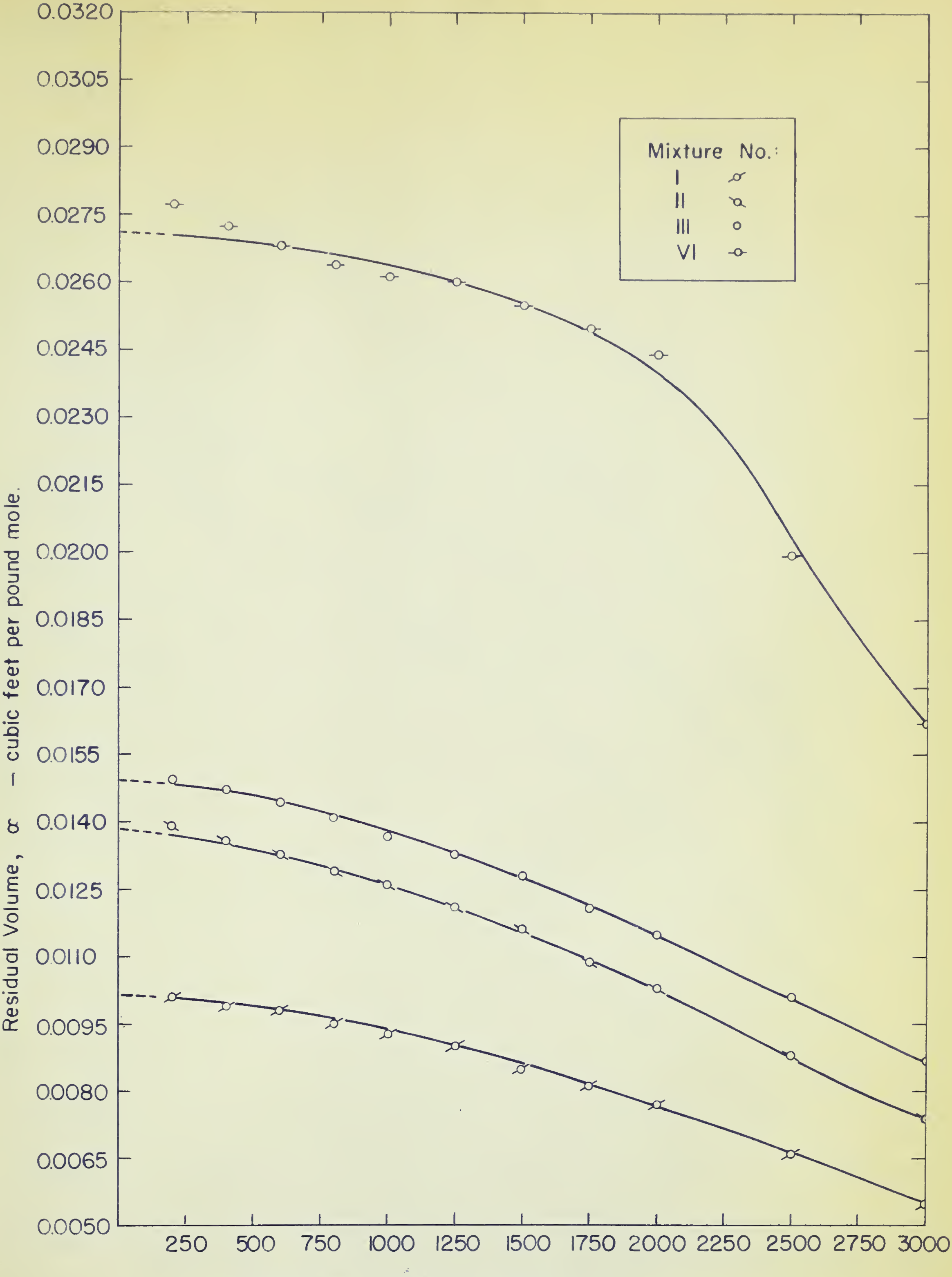
Kay's method, also, of the "pseudoreduced" conditions, provides a satisfactory means of correlating compressibility factors of mixtures in a similar manner.

For thermodynamic calculations, however, these correlations are not accurate enough and, in addition, are not well adapted to graphical methods. Neither is any of the usual equations of state sufficiently accurate over wide ranges to permit accurate determination of first or higher differential coefficients.

In the calculation of S, H, Cp, μ, etc., when p and T are the independent variables, the coefficients $(\frac{\partial V}{\partial T})_p$ and $(\frac{\partial^2 V}{\partial T^2})_p$ must be evaluated. Deming and Shupe (18) used among other residual quantities the "residual" volume $\alpha = \frac{RT}{P} - V$ from which several equations can be obtained by differentiation, yielding values for the above differential coefficients.

An inherent feature of the residual volume correlation is its ability in describing very accurately the behavior of a gas at relatively low pressures.

Figures (12, 13 & 14) and Tables (XV,XVI & XVII) in the appendix represent such a correlation for several of the experimentally studied ternary mixtures. The experimental compressibility factors employed in the calculation of the residual volume , were obtained from smoothed experimental curves.



Pressure – pounds per square inch.

Figure - 12. Residual Volume Correlation of the Experimental Data of the Ternary Systems at 160 °F.

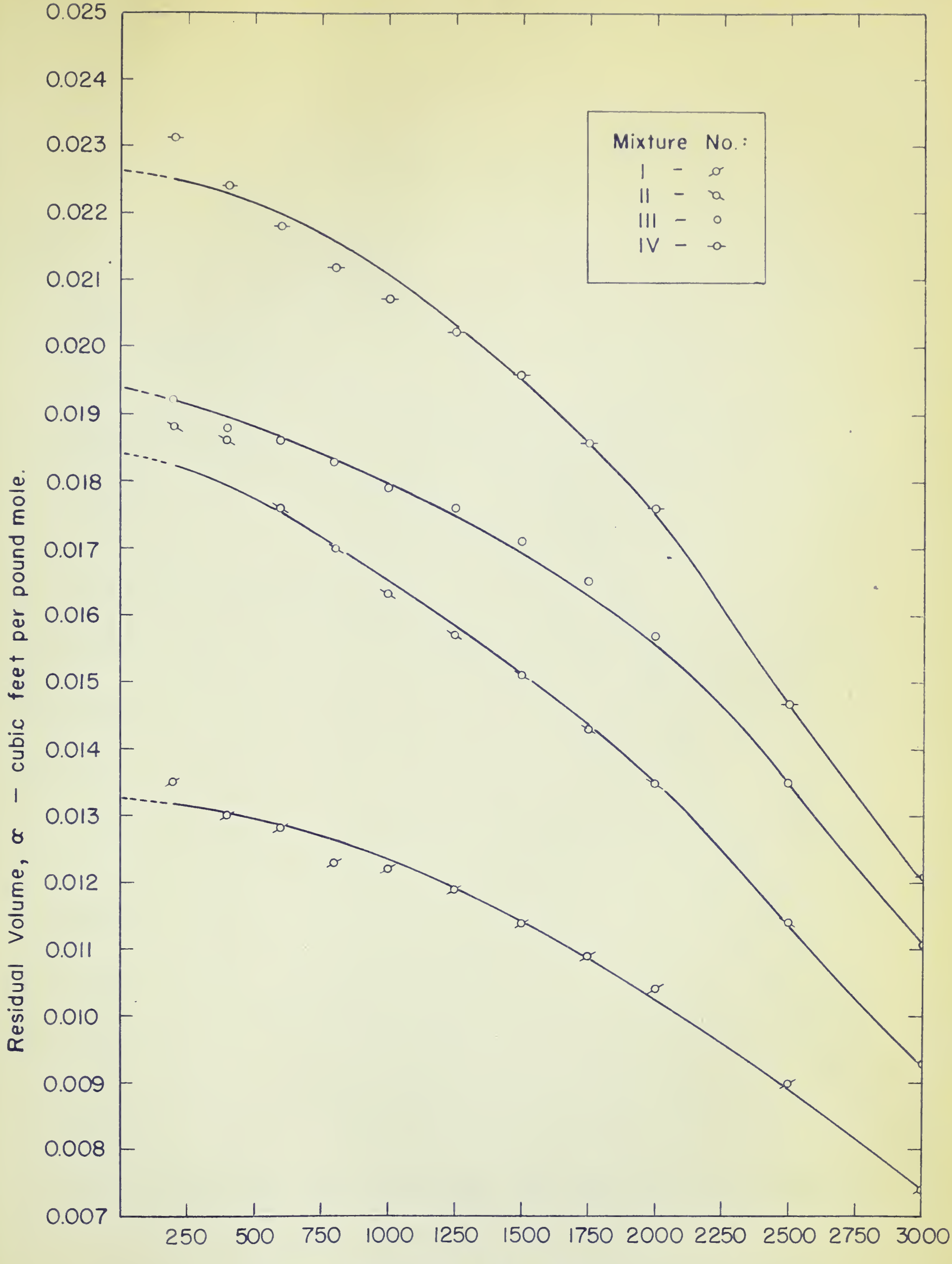


Figure - 13. Residual Volume Correlatiom of the Experimental Data of the Ternary Systems at 100 °F.

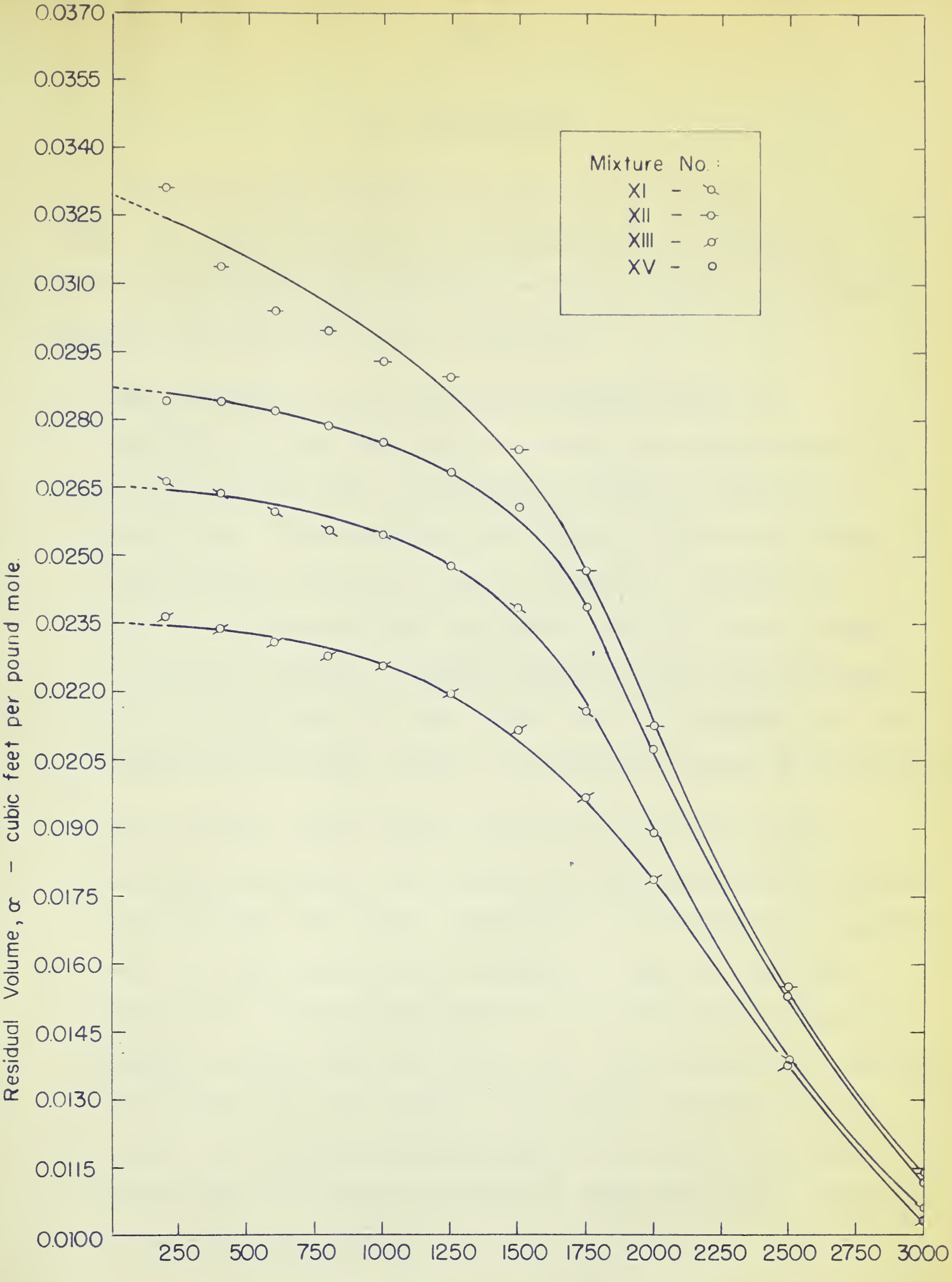


Figure-14. Residual Volume Correlation of the Experimental Data of the Ternary Systems at 40 °F.

I. CONCLUSIONS

Following the discussion of the results and the comparison of the experimental compressibility factors to those calculated by the mentioned methods a summary of arising conclusions would have been as follows:

1. The temperature during the investigation plays an important role in the question whether the compressibility of the mixtures can be described by means of methods of prediction. Kay's method could be applicable with rather satisfactory results for some engineering problems for the temperatures of 160° and 100°F. over the entire range of pressure studied. Methods based on additivity concepts are not valid even for the lower range of pressure. At the temperature of 40°F. there is no adequate method of prediction.

2. The pressure, also, has an important influence on the discrepancy between the calculated compressibilities and the experimental. At higher pressures the discrepancy is greater, save the case when Amagat's method is applied, and this phenomenon is more pronounced as the temperature decreases. Amagat's method does not follow the rule exhibiting a maximum discrepancy over the range of pressures for which at the temperature of the investigation one or more of the pure components are assumed as being in their two phase region or in the liquid phase.

3. The composition of the mixtures, also, is very significant.. Over the entire range of pressure and for the three temperatures of the investigation it can be said that the discrepancy increases as the methane content in the system decreases.

The limited number of runs, for which an appreciable variation of carbon dioxide and hydrogen sulfide content was achieved in this work is not sufficient to permit a discussion. A future investigation describing the individual role of hydrogen sulfide and carbon dioxide in the compressibility of the ternary system would be of some significance.

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APPENDIX

1. TABULATED EXPERIMENTAL AND CALCULATED DATA
2. SAMPLE CALCULATIONS

Table I

Phase Composition Data

P = 1330 PSIA T = 160°F.

Test	Total System Composition			Vapor Phase Composition			Liquid Phase Composition		
No.	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
A-3	.732	.109	.159	.704	.126	.170	.848	.064	.088
A-8	.703	.155	.142	.699	.162	.139	.770	.123	.107
A-11	.696	.203	.101	.676	.224	.100	.718	.197	.085
A-16	.811	.048	.141	.724	.066	.210	.903	.023	.074
A-9	.657	.250	.093	one phase region (vapor)					
A-10	.607	.307	.086	one phase region (vapor)					

Table II

Equilibrium Ratios at Regular Values of the Parameter C

P = 1330 PSIA T = 160°F.

Parameter	Vapor Phase Composition			Liquid Phase Composition			Experimental Equil. ratios		
C	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
0.1	.727	.028	.255	.905	.012	.085	.807	2.33	2.90
0.2	.723	.056	.221	.882	.028	.090	.820	1.95	2.45
0.4	.708	.117	.175	.823	.084	.093	.857	1.40	1.87
0.6	.689	.186	.125	.757	.143	.100	.910	1.30	1.25

Table III

1. Experimental and Theoretical Equilibrium Ratios
2. Calculated Activity Coefficient Ratios

Parameter	Experimental K Values			Theoretical K Values			Exper. Activity Coeff. Ratios		
C	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
0.1	.807	2.33	2.90	.750	1.415	7.04	1.075	1.645	.412
0.2	.820	1.95	2.45	.750	1.415	7.04	1.090	1.376	.348
0.4	.857	1.40	1.87	.750	1.415	7.04	1.135	.990	.266
0.6	.910	1.30	1.25	.750	1.415	7.04	1.210	.920	.177

Table No. IV. Experimental Compressibility Factors of the Hydrogen Sulfide-Carbon Dioxide system at 160°F.

Mixture No.:	1		2		3	
Mole Fraction : H_2S	.1775		.2035		.6025	
	P_{psia}	z	P_{psia}	z	P_{psia}	z
	218	.949	317	.923	147	.941
	263	.939	344	.921	165	.944
	290	.927	395	.905	183	.938
	336	.919	443	.889	235	.918
	388	.901	536	.863	285	.906
	435	.887	632	.834	335	.888
	479	.874	828	.780	431	.857
	577	.853	1024	.717	530	.833
	725	.806	1229	.650	630	.806
	823	.778	1525	.530	828	.740
	1040	.720	1795	.445	1026	.669
	1229	.657			1232	.559
	1525	.554				

Table No. V. Experimental Compressibility Factors of the Methane-Hydrogen Sulfide-Carbon Dioxide System at 160°F.

Mixture No.:		I		II		III		VI		V	
Mole	H_2S	.0392		.1252		.2331		.5256		.0857	
:	CO_2	.1814		.1751		.1538		.1044		.3660	
Fraction	CH_4	.7794		.6997		.6131		.3700		.5483	
		P_{psia}	z	P_{psia}	z	P_{psia}	z	P_{psia}	z	P_{psia}	z
		941	.926	681	.916	392	.955	239	.935	153	.971
		1040	.917	740	.912	439	.943	288	.924	167	.965
		1140	.908	839	.901	538	.934	338	.911	187	.960
		1287	.899	942	.893	637	.918	432	.896	214	.956
		1439	.887	1036	.879	732	.911	527	.864	238	.949
		1632	.876	1235	.862	832	.895	630	.841	286	.942
		1824	.860	1444	.846	1033	.876	840	.795	339	.934
		2028	.859	1742	.826	1230	.857	1131	.726	432	.918
		2406	-	2038	.809	1440	.833	1433	.664	536	.904
		2902	.846	2441	.795	1728	.809	1741	.590	678	.885
				2944	.795	2040	.789	2024	.544	834	.865
						2452	.770			1028	.848
						2832	.762				

Mixture No.:		Ia		IIa	
Mole	H_2S	.0426		.1118	
:	CO_2	.1818		.1728	
Fraction	CH_4	.7756		.7154	
		303	.979	128	.998
		341	.973	140	.994
		438	.959	164	.987
		538	.948	188	.976
		640	.940	236	.966
		834	.925	334	.956
		1032	.904	434	.941
		1230	.894	633	.914
		1530	.874	833	.897
		1827	.857		

Table No. VI. Experimental Compressibility Factors of the Methane-Hydrogen Sulfide-Carbon Dioxide System at 100°F.

Mixture No.:	I		II		III		IV	
Mole H_2S	.0392		.1252		.2331		.1989	
: CO_2	.1814		.1751		.1538		.2781	
Fraction CH_4	.7794		.6997		.6131		.5230	
	P_{psia}	z	P_{psia}	z	P_{psia}	z	P_{psia}	z
	830	.897	595	.897	341	.942	393	.913
	893	.889	641	.887	390	.933	440	.899
	990	.878	734	.873	447	.921	539	.882
	1087	.867	834	.861	536	.904	636	.861
	1239	.846	936	.842	633	.883	734	.842
	1432	.827	1031	.828	733	.866	830	.821
	1731	.800	1231	.800	882	.842	1029	.784
	2032	-	1442	-	1027	.816	1231	.745
	2335	.772	1641	.756	1221	.782	1438	.710
	2628	.768	1932	.729	1434	.746	1639	.682
	2936	.769	2224	.715	1631	.718	1929	.645
			2540	,707	1923	.687	2233	.625
			2930	.711	2227	.665	2560	.623
					2531	.655	2910	.622
					2916	.669		

Mixture No.:	Ia		IIa	
Mole H_2S	.0426		.1118	
: CO_2	.1818		.1728	
Fraction CH_4	.7756		.7154	
	270	.967	115	.977
	293	.961	148	.974
	339	.957	185	.954
	390	.954	238	.943
	439	.938	333	.929
	489	.930	432	.916
	588	.920	634	.881
	734	.906	830	.862
	884	.882		
	1031	.865		
	1239	.850		

Table No.VII. Experimental Compressibility Factors of the Methane-Hydrogen Sulfide- Carbon Dioxide System at 40°F.

Mixture No.:		XI		XII		XIII		XV		XVI	
Mole	H_2S	.2440		.2095		.1338		.1475		.1178	
:	CO_2	.1575		.2760		.1762		.2965		.2365	
Fraction	CH_4	.5985		.5145		.6900		.5560		.6457	
		P_{psia}	z	P_{psia}	z	P_{psia}	z	P_{psia}	z	P_{psia}	z
		298	.890	353	.872	536	.855	442	.872	554	.856
		340	.870	411	.850	632	.829	488	.857	634	.831
		434	.853	486	.833	734	.807	585	.832	729	.809
		533	.830	628	.790	833	.781	736	.783	836	.784
		630	.804	716	.763	931	.757	871	.737	1024	.733
		734	.779	835	.727	1064	.722	1017	.690	1222	.686
		824	.754	1026	.666	1232	.686	1243	.611	1536	.617
		1023	.699	1236	.597	1511	.630	1490	.548	1827	.582
		1215	.648	1430	.537	1807	.594	1748	.517	2105	.575
		1509	.585	1807	.500	2138	.585	2122	.531	2453	.594
		1821	.559	2159	.517	2449	.597	2557	.555	2832	.619
		2414	.589	2479	.545	2806	.623	2912	.598		
				2689	.571						

Table No. VIII. Prediction of the Compressibility of the Ternary System by Amagat.

$$z_m = z_A y_A + z_B y_B + z_C y_C + \ldots .$$

1		2			3			4		5	6
Mixture No.		H_2S			CO_2			CH_4			Exper.
	y	z	zy	y	z	zy	y	z	zy	zy	z
		Temperature 160°F.			-		Pressure 500 psia.				
I	.0409	.8025	.0328	.1816	.8930	.1622	.7775	.9680	.7526	.9476	.9570
II	.1185	.8025	.0951	.1740	.8930	.1554	.7075	.9680	.6849	.9354	.9400
III	.2331	.8025	.1871	.1538	.8930	.1373	.6131	.9680	.5935	.9179	.9365
VI	.5256	.8025	.4218	.1044	.8930	.0932	.3700	.9680	.3582	.8732	.8725
		Temperature 160°F.			-		Pressure 1000 psia.				
I	.0409	.1267	.0052	.1816	.7590	.1379	.7775	.9410	.7316	.8747	.9130
II	.1185	.1267	.0150	.1740	.7590	.1321	.7075	.9410	.6658	.8130	.8820
III	.2331	.1267	.0296	.1538	.7590	.1167	.6131	.9410	.5769	.7231	.8710
VI	.5256	.1267	.0666	.1044	.7590	.0793	.3700	.9410	.3483	.4942	.7550
		Temperature 160°F.			-		Pressure 2000 psia.				
I	.0409	.2378	.0097	.1816	.4790	.0870	.7775	.9109	.7082	.8049	.8560
II	.1185	.2378	.0282	.1740	.4790	.0834	.7075	.9109	.6445	.7561	.8070
III	.2331	.2378	.0554	.1538	.4790	.0737	.6131	.9109	.5585	.6876	.7850
VI	.5256	.2378	.1250	.1044	.4790	.0500	.3700	.9109	.3371	.5121	.5440
		Temperature 160°F.			-		Pressure 3000 psia.				
I	.0409	.3440	.0145	.1816	.4790	.0870	.7775	.9165	.7125	.8140	.8470
II	.1185	.3440	.0408	.1740	.4790	.0834	.7075	.9165	.6484	.7725	.7920
III	.2331	.3440	.0801	.1538	.4790	.0737	.6131	.9165	.5619	.7157	.7550
VI	.5256	.3440	.1808	.1044	.4790	.0500	.3700	.9165	.3392	.5700	.5460

Table No. IX.

1		2			3			4		5	6
			Temperature 100°F.		-		Pressure 500 psia.				
I	.0409	.0635	.0026	.1816	.8370	.1520	.7775	.9510	.7394	.8940	.9360
II	.1185	.0635	.0075	.1740	.8370	.1456	.7075	.9510	,6728	.8259	.9160
III	.2331	.0635	.0148	.1538	.8370	.1287	.6131	.9510	.5831	.7266	.9110
			Temperature 100°F.		-		Pressure 1000 psia.				
I	.0409	.1200	.0049	.1816	.5815	.1056	.7775	.9070	.7052	.8157	.8740
II	.1185	.1200	.0142	.1740	.5815	.1012	.7075	.9070	.6417	,7571	.8350
III	.2331	,1200	.0280	.1538	.5815	.0894	.6131	.9070	.5561	.6735	.8215
			Temperature 100°F.		-		Pressure 2000 psia.				
I	.0409	.2335	.0096	.1816	.3015	,0548	.7775	.8520	.6624	.7268	.7865
II	.1185	,2335	.0277	.1740	.3015	.0525	.7075	.8520	.6028	.6830	.7235
III	.2331	.2335	.0544	.1538	.3015	.0464	.6131	.8520	.5224	.6232	.6840
			Temperature 100°F.		-		Pressure 3000 psia.				
I	.0409	.3435	.0141	.1816	.4100	.0745	.7775	.8550	.6648	.7534	.7735
II	.1185	.3435	.0407	.1740	.4100	.0713	.7075	.8550	.6049	.7169	.7140
III	.2331	.3435	.0801	.1538	.4100	.0631	,6131	.8550	.5242	.6874	.6625

Temperature 40°F. - Pressure 250 psia.

XI	.2440	.0350	.0085	.1575	.8875	.1398	.5985	.9615	.5755	.7238	.9210
XII	.2095	.0350	.0073	.2760	.8875	.2450	.5145	.9615	.4947	.7470	.9190
XIII	.1338	.0350	.0047	.1762	.8875	.1564	.6900	.9615	.6634	.8245	.9350
XV	.1475	.0350	.0052	.2965	.8875	.2631	.5560	.9615	.5346	.8029	.9275
XVI	.1178	.0350	.0041	.2365	.8875	.2099	.6457	.9615	.6208	.8348	.9350

Temperature 40°F. - Pressure 500 psia.

XI	.2440	.0640	.0156	.1575	.0860	.0135	.5985	.9230	.5524	.5815	.8450
XII	.2095	.0640	.0134	.2760	.0860	.0237	.5145	.9230	.4749	.5120	.8375
XIII	.1338	.0640	.0086	.1762	.0860	.0152	.6900	.9230	.6369	.6607	.8700
XV	.1475	.0640	.0094	.2965	.0860	.0255	.5560	.9230	.5132	.5481	.8550
XVI	.1178	.0640	.0075	.2365	.0860	.0203	.6457	.9230	.5960	.6238	.8700

Temperature 40°F. - Pressure 1000 psia.

XI	.2440	.1250	.0305	.1575	.1475	.0232	.5985	.8500	.5087	.5624	.7060
XII	.2095	.1250	.0262	.2760	.1475	.0407	.5145	.8500	.4373	.5042	.6750
XIII	.1338	.1250	.0167	.1762	.1475	.0260	.6900	.8500	.5865	.6292	.7375
XV	.1475	.1250	.0184	.2965	.1475	.0437	.5560	.8500	.4726	.5347	.6910
XVI	.1178	.1250	.0147	.2365	.1475	.0349	.6457	.8500	.5488	.5984	.7375

Temperature 40°F. - Pressure 2000 psia.

XI	.2440	.2400	.0586	.1575	.2700	.0425	.5985	.7585	.4540	.5551	.5625
XII	.2095	.2400	.0503	.2760	.2700	.0745	.5145	.7585	.3902	.5150	.5060
XIII	.1338	.2400	.0321	.1762	.2700	.0476	.6900	.7585	.5234	.6031	.5850
XV	.1475	.2400	.0354	.2965	.2700	.0801	.5560	.7585	.4217	.5372	.5200
XVI	.1178	.2400	.0283	.2365	.2700	.0639	.6457	.7585	.4898	.5820	.5725

Temperature 40°F. - Pressure 3000 psia.

XI	.2440	.3560	.0869	.1575	.3930	.0619	.5985	.7785	.4659	.6147	.6375
XII	.2095	.3560	.0746	.2760	.3930	.1085	.5145	.7785	.4005	.5836	.6110
XIII	.1338	.3560	.0476	.1762	.3930	.0692	.6900	.7785	.5372	.6540	.6420
XV	.1475	.3560	.0525	.2965	.3930	.1165	.5560	.7785	.4328	.6018	.6135
XVI	.1178	.3560	.0419	.2365	.3930	.0929	.6457	.7785	.5027	.6375	.6400

Table XI. Prediction of the Compressibility of the Ternary System by Kay.

Temperature 160°F.

	P_c psia.	T_c °R	y_I	y_{II}	y_{III}	y_{VI}
H_2S	1306	672.7	.0409	.1185	.2331	.5256
CO2	1072	549.8	.1816	.1740	.1538	.1044
CH_4	673	341.5	.7775	.7075	.6131	.3700

Mixture No.	H_2S yP_c	H_2S yT_c	CO_2 yP_c	CO_2 yT_c	CH_4 yP_c	CH_4 yT_c	$\sum yP_c = P_{cm}$	$\sum yT_c = T_{cm}$	$T_{rm} = \frac{T}{T_{cm}}$
I	53.4	27.5	194.5	99.4	522.9	266.6	770.8	393.5	1.58
II	154.4	79.7	186.2	95.2	476.6	242.6	817.2	417.5	1.49
III	304.3	156.7	165.3	84.2	413.0	210.2	882.6	451.1	1.37
VI	686.8	353.3	111.7	57.2	249.0	126.9	1047.5	537.4	1.15

Mixture No.	Pressure 1000 psia. $P_{rm}=\frac{P}{P_{cm}}$	z_m	z_{exp}	Pressure 2000 psia. $P_{rm}=\frac{P}{P_{cm}}$	z_m	z_{exp}	Pressure 3000 psia. $P_{rm}=\frac{P}{P_{cm}}$	z_m	z_{exp}
I	1.30	.915	.913	2.60	.850	.856	3.90	.845	.847
II	1.22	.900	.882	2.44	.815	.807	3.66	.800	.792
III	1.13	.865	.871	2.26	.760	.785	3.39	.720	.755
VI	0.96	.770	.755	1.92	.520	.544	2.88	.500	.525

Table No. XII. Prediction of the Compressibility of the Ternary System by Kay.

Temperature 100°F.

	P_c psia.	T_c °R	y_I	y_{II}	y_{III}
H_2S	1306	672.7	.0409	.1185	.2331
CO_2	1072	549.8	.1816	.1740	.1538
CH_4	673	341.5	.7775	.7075	.6131

Mixture No.	H_2S		CO_2		CH_4		$\sum yP_c = P_{cm}$	$\sum yT_c = T_{cm}$	$T_{rm} = \frac{T}{T_{cm}}$
	yP_c	yT_c	yP_c	yT_c	yP_c	yT_c			
I	53.4	27.5	194.5	99.4	552.9	266.6	770.8	393.3	1.42
II	154.4	79.7	186.2	95.2	476.6	242.6	817.2	417.5	1.34
III	304.4	156.7	165.3	84.2	413.0	210.2	882.6	451.1	1.24

Mixture No.	Pressure 1000 psia.			Pressure 2000 psia.			Pressure 3000 psia.		
	$P_{rm} = \frac{P}{P_{cm}}$	z_m	z_{exp}	$P_{rm} = \frac{P}{P_{cm}}$	z_m	z_{exp}	$P_{rm} = \frac{P}{P_{cm}}$	z_m	z_{exp}
I	1.30	.860	.874	2.60	.765	.784	3.90	.760	.768
II	1.22	.840	.830	2.44	.710	.721	3.66	.705	.709
III	1.13	.795	.813	2.26	.610	.675	3.39	.615	.653

Table No. XIII. Prediction of the Compressibility of the Ternary System by Kay.

Temperature 40°F.

	P_c psia.	T_c °R	y_I	y_{II}	y_{III}	y_V	y_{VI}
H_2S	1306	672.7	.2440	.2095	.1338	.1475	.1178
CO_2	1072	549.8	.1575	.2760	.1762	.2965	.2365
CH_4	673	341.5	.5985	.5145	.6900	.5560	.6457

Mixture	H_2S		CO_2		CH_4				
No.	yP_c	yT_c	yP_c	yT_c	yP_c	yT_c	$\sum yP_c = P_{cm}$	$\sum yT_c = T_{cm}$	$T_{rm}=\frac{T}{T_{cm}}$
XI	318.7	164.0	168.8	86.2	402.8	205.2	890.3	455.5	1.10
XII	273.6	140.8	295.9	151.0	346.3	176.4	915.8	468.2	1.07
XIII	174.7	90.0	188.9	96.5	464.4	236.5	828.0	423.0	1.18
XV	192.6	99.2	317.8	162.4	374.2	190.8	884.6	452.4	1.11
XVI	153.8	79.2	253.3	129.4	434.6	221.4	841.9	430.0	1.16

Mixture	Pressure 500 psia.			Pressure 1000 psia.			Pressure 2000 psia.			Pressure 3000 psia.		
No.	$P_{rm}=\frac{P}{P_{cm}}$	z_m	z_{exp}	$P_{rm}=\frac{P}{P_{cm}}$	z_m	z_{exp}	$P_{rm}=\frac{P}{P_{cm}}$	z_m	z_{exp}	$P_{rm}=\frac{P}{P_{cm}}$	z_m	z_{exp}
XI	.560	.848	.845	1.12	.650	.704	2.24	.405	.561	3.36	.510	.630
XII	.545	.835	.838	1.09	.615	.674	2.18	.380	.506	3.27	.490	.602
XIII	.608	.875	.870	1.22	.720	.738	2.44	.525	.584	3.66	.590	.640
XV	.565	.850	.855	1.13	.665	.696	2.26	.425	.516	3.39	.520	.608
XVI	.595	.865	.870	1.19	.705	.740	2.38	.495	.575	3.57	.560	.634

Table No. XIV. Percent Deviation of the Calculated Compressibility of the Ternary

System from the Experimental.

Mixture No.		Pressure 500psia.		Pressure 1000psia.			Pressure 2000psia.			Pressure 3000psia.	
	Exper. z	Dev. % Amagat	Exper. z	Dev. % Amagat	Kay	Exper. z	Dev. % Amagat	Kay	Exper. z	Dev. % Amagat	Kay
Temperature 160°F.											
I	.957	-0.94	.913	-4.16	+0.22	.856	-5.96	-0.7	.847	-3.90	-0.24
II	.940	-0.53	.882	-7.82	+2.04	.807	-6.32	+1.0	.792	-2.48	+1.00
III	.937	-2.00	.871	-17.00	-0.69	.785	-12.40	-3.2	.755	-5.17	-4.60
VI	.873	0.00	.755	-34.60	+2.00	.544	-5.88	-4.4	.546	+4.40	-4.80
Temperature 100°F.											
I	.936	-4.5	.874	-6.64	-1.6	.787	-7.62	-2.4	.774	-2.71	-1.0
II	.916	-9.8	.835	-9.34	+1.2	.724	-5.66	-1.5	.714	+0.42	-0.6
III	.911	-20.2	.822	-18.00	-2.2	.684	-8.92	- .6	.663	+3.62	-5.8
Temperature 40°F.											
XI	.845	-31.1	.706	-20.4	-7.7	.563	-1.4	-27.8	.638	-3.6	-19.0
XII	.838	-38.9	.675	-25.3	-8.8	.506	+1.8	-24.9	.611	-4.4	-18.6
XIII	.870	-24.0	.738	-14.8	-2.4	.585	+3.1	-11.0	.642	+1.9	-8.6
XV	.855	-35.9	.691	-22.6	-4.5	.520	+3.3	-17.6	.614	-2.0	-14.5
XVI	.870	-28.3	.738	-19.0	-4.7	.573	+1.6	-13.9	.640	-0.3	-11.7

Table No. XV. Residual Volume Correlation of the Ternary System at 160°F.

1	2	3		4		5		6	
Mixture No.:		I	(*)	II		III		VI	
Pressure psia	$\frac{RT}{P}$(*)	(1-z)	$\alpha=(1-z)\frac{RT}{P}$	(1-z)	$\alpha=(1-z)\frac{RT}{P}$	(1-z)	$\alpha=(1-z)\frac{RT}{P}$	(1-z)	$\alpha=(1-z)\frac{RT}{P}$
200	.5330	.019	.0101	.026	.0139	.028	.0149	.052	.0277
400	.2665	.037	.0099	.051	.0136	.055	.0147	.102	.0272
600	.1777	.055	.0098	.075	.0133	.081	.0144	.151	.0268
800	.1333	.071	.0095	.097	.0129	.106	.0141	.199	.0264
1000	.1066	.087	.0093	.118	.0126	.129	.0137	.245	.0261
1250	.0853	.105	.0090	.142	.0121	.156	.0133	.304	.0260
1500	.0711	.120	.0085	.163	.0116	.180	.0128	.359	.0255
1750	.0609	.133	.0081	.179	.0109	.199	.0121	.410	.0250
2000	.0533	.144	.0077	.193	.0103	.215	.0115	.456	.0244
2500	.0426	.154	.0066	.207	.0088	.237	.0101	.468	.0199
3000	.0355	.154	.0055	.208	.0074	.245	.0087	.454	.0162

(*) Values expressed in cubic feet per pound mole.

Table No.XVI. Residual Volume Correlation of the Ternary System at 100°F.

1	2	3		4		5		6	
Mixture No.:		I		II		III		IV	
200	.4814	.028	.0135	.039	.0188	.040	.0192	.048	.0231
400	.2407	.054	.0130	.077	.0186	.078	.0188	.093	.0224
600	.1605	.080	.0128	.110	.0176	.116	.0186	.136	.0218
800	.1204	.103	.0123	.141	.0170	.152	.0183	.176	.0212
1000	.0963	.126	.0122	.170	.0163	.187	.0179	.214	.0207
1250	.0770	.153	.0119	.204	.0157	.229	.0176	.261	.0202
1500	.0642	.178	.0114	.234	.0151	.268	.0171	.303	.0196
1750	.0550	.199	.0109	.260	.0143	.300	.0165	.338	.0186
2000	.0481	.216	.0104	.279	.0135	.325	.0157	.365	.0176
2500	.0385	.232	.0090	.294	.0114	.349	.0135	.384	.0147
3000	.0321	.231	.0074	.291	.0093	.347	.0111	.380	.0121

Table No.XVII. Residual Volume Correlation of the Ternary System at 40°F.

1	2	3		4		5		6	
Mixture No.:		XI		XII		XIII		XV	
200	.4300	.062	.0266	.077	.0331	.055	.0237	.066	.0284
400	.2150	.123	.0264	.146	.0314	.109	.0234	.132	.0284
600	.1433	.181	.0260	.212	.0304	.161	.0231	.197	.0282
800	.1075	.239	.0256	.278	.0300	.212	.0228	.260	.0279
1000	.0860	.296	.0255	.341	.0293	.262	.0226	.320	.0276
1250	.0688	.361	.0248	.420	.0290	.318	.0220	.390	.0269
1500	.0573	.415	.0239	.478	.0274	.368	.0212	.454	.0261
1750	.0491	.440	.0216	.502	.0247	.401	.0197	.484	.0239
2000	.0430	.439	.0189	.494	.0213	.416	.0179	.484	.0208
2500	.0344	.406	.0139	.453	.0155	.398	.0137	.446	.0154
3000	.0287	.371	.0106	.398	.0114	.360	.0103	.392	.0112

Sample Calculation - Part 1

Run A - 8

Equilibrium condition : T = 160 Degrees Fahrenheit; P = 1330 pounds per square inch absolute

The desired total composition in the two phase region was:

H_2S = .72 mole fraction

CH_4 = .13 mole fraction

CO_2 = .15 mole fraction

(1) Addition of H_2S to equilibrium cell

P = 400 psia.

T = 161 Degrees Fahrenheit = 621 Degrees Rankin

V = 71.0 c.c.

z = 0.851

$$R = 670 \frac{\text{lb} \quad \text{c.c.}}{\text{in}^2 \cdot {}^\circ\text{R} \cdot \text{gm. mole}}$$

$$n = \frac{PV}{zRT} = \frac{400 \times 71.0}{0.851 \times 670 \times 621} = .0801 \text{ gm. moles.}$$

(2) Addition of CH_4 to measuring cell

(a) Moles of CH_4 required:

$$n = \frac{13}{72} \times .0801 = .0145 \text{ gm. moles.}$$

CH_4 was to be added to the measuring cell at the pressure of 200 psia and at a cell temperature of 72 degrees F. At these conditions the compressibility factor was 0.975. The volume required in the measuring cell was:

$$V = \frac{nzRT}{P} = \frac{0.0145 \times 0.975 \times 670 \times 532}{200} = 25.15 \text{ cc.}$$

(b) Actual quantity of CH_4 added:

P = 200 psia.

T = 72 Degrees F. = 532 Degrees R

V = 28.2 c.c

$$n = \frac{PV}{zRT} = \frac{200 \times 28.2}{670 \times 0.975 \times 532} = .0162 \text{ gm. moles.}$$

(3) Addition of CO_2 to measuring cell

(a) Moles of CO_2 required:

$$\frac{n}{n + .0801 + .0162} = .15$$

$$n = .0137 \text{ gm. moles.}$$

CO_2 was to be added to the measuring cell at a pressure of 100 psia. and at a cell temperature of 72 Degrees F. At these conditions the compressibility factor of CO_2 was 0.958. The volume required in the measuring cell, then, was:

$$V = \frac{nzRT}{P} = \frac{.0137 \times 0.958 \times 670 \times 532}{100} = 46.8 \text{ c.c}$$

(b) Actual quantity of CO_2 added:

P = 100 psia.

T = 72 Degrees F. = 532 Degrees R

V = 60.0 c.c

$$n = \frac{PV}{zRT} = \frac{100 \times 60.0}{0.958 \times 670 \times 532} = .0176 \text{ gm. moles.}$$

(4) Total System Composition:

	Moles	Mole Fraction
H_2S :	.0801	.7032
CH_4 :	.0162	.1423
CO_2 :	.0176	.1545

(5) Composition of Phases at Equilibrium as Determined by Analysis:

	Gas Phase	Liquid Phase
H_2S	.699	.770
CH_4	.1395	.1075
CO_2	.1615	.1225

Sample Calculation of Predicting the Compressibility Factor by the Gilliland's Method

Mixture chosen: No. 2 binary of carbon dioxide-hydrogen sulfide.

Temperature = 160°F., Pressure 1000 psia.

Then, experimental compressibility factor: .735.

We assume a number of compressibility factors including the experimentally found.

Choose: $z_1 = .400$

$z_2 = .600$

$z_3 = .800$

We then calculate the molal volume occupied by the gas mixture of the chosen compressibility factors at the above conditions.

$$z_1 = 0.4 \quad V_1 = \frac{0.4 \times 620 \times 670}{1000} = .1662 \text{ lit/gmole.}$$

$$z_2 = 0.6 \quad V_2 = \frac{0.6}{0.4} V_1 = .2493 \text{ lit/gmole.}$$

$$z_3 = 0.8 \quad V_3 = 2V_1 = .3324 \text{ lit/gmole.}$$

Step 1

We then calculate the pressure exerted by each of the components of the mixture separately if they were occupying the above found molal volumes at the temperature of 160°F.

General equation to be used:

$$P_r = z \frac{RT}{PcV} \quad \text{where}$$

$$R = .082 \frac{\text{atm. liters}}{\text{gmol.°K}} \quad T = (160°\text{F.}) \text{ or } 344°\text{K and}$$

$$Pc^{H_2S} = 88.9 \text{ atm.} \qquad Pc^{CO_2} = 73.0 \text{ atm.}$$

The procedure to obtain P_r required a trial and error solution using the reduced conditions - compressibility charts (12) for the previously found values of V. The obtained values of P_r for each of the components at the three values of V are shown in the following table:

Table a.

I CO_2 : $P_r = \frac{.082 \times 344}{73.0\ V} z = .3864 \frac{z}{V}$, $T_r = \frac{344}{304.1} = 1.13$

II H_2S : $P_r = \frac{.082 \times 344}{88.9\ V} z = .3173 \frac{z}{V}$, $T_r = \frac{344}{373.4} = .92$

I $V_1 = .1662$ $P_{r1} = 2.32, z_1 = 1.35$

$V_2 = .2493$ $P_{r2} = 1.55, z_2 = 1.07$

$V_3 = .3324$ $P_{r3} = 1.16, z_3 = .88$

II $V_1 = .1662$ $P_{r1} = 1.91, z_1 = .70$

$V_2 = .2493$ $P_{r2} = 1.27, z_2 = .66$

$V_3 = .3324$ $P_{r3} = .95, z_3 = .63$ and thus

we obtain Table b.

Table b.

	$V_1 = .1662$	$V_2 = .2493$	$V_3 = .3324$
CO_2 : $P = P_r \; P_c$	98.6	78.1	64.2
H_2S : $P = P_r \; P_c$	62.2	58.7	56.0

Step 2

From Figure (11), representing V_r vs$(\phi_2)_r$ we get values of $(\phi_2)_r$ corresponding to the chosen values of V_r

CO_2

$$V_{r1} = \frac{V_1}{V_c} = \frac{.1662}{.0957} = 1.74 \quad \phi_{2r1} = 2.17$$

$$V_{r2} = \frac{V_2}{V_c} = \frac{.2493}{.0957} = 2.61 \quad \phi_{2r2} = 1.05$$

$$V_{r3} = \frac{V_3}{V_c} = \frac{.3324}{.0957} = 3.47 \quad \phi_{2r3} = .63$$

H_2S

$$V_{r1} = \frac{V_1}{V_c} = \frac{.1662}{.0977} = 1.70 \quad \phi_{2r1} = 1.280$$

$$V_{r2} = \frac{V_2}{V_c} = \frac{.2493}{.0977} = 2.55 \quad \phi_{2r2} = 0.300$$

$$V_{r3} = \frac{V_3}{V_c} = \frac{.3324}{.0977} = 3.40 \quad \phi_{2r3} = 0.105$$

So, we finally obtain values of ϕ_2 for each of the components for the chosen compressibility factors.

	$V_1 = .1662$	$V_2 = .2493$	$V_3 = .3324$
CO_2 : $\phi_2 = \phi_{2r} \; P_c$	158.4	76.7	46.0
H_2S : $\phi_2 = \phi_{2r} \; P_c$	114.0	26.7	9.4

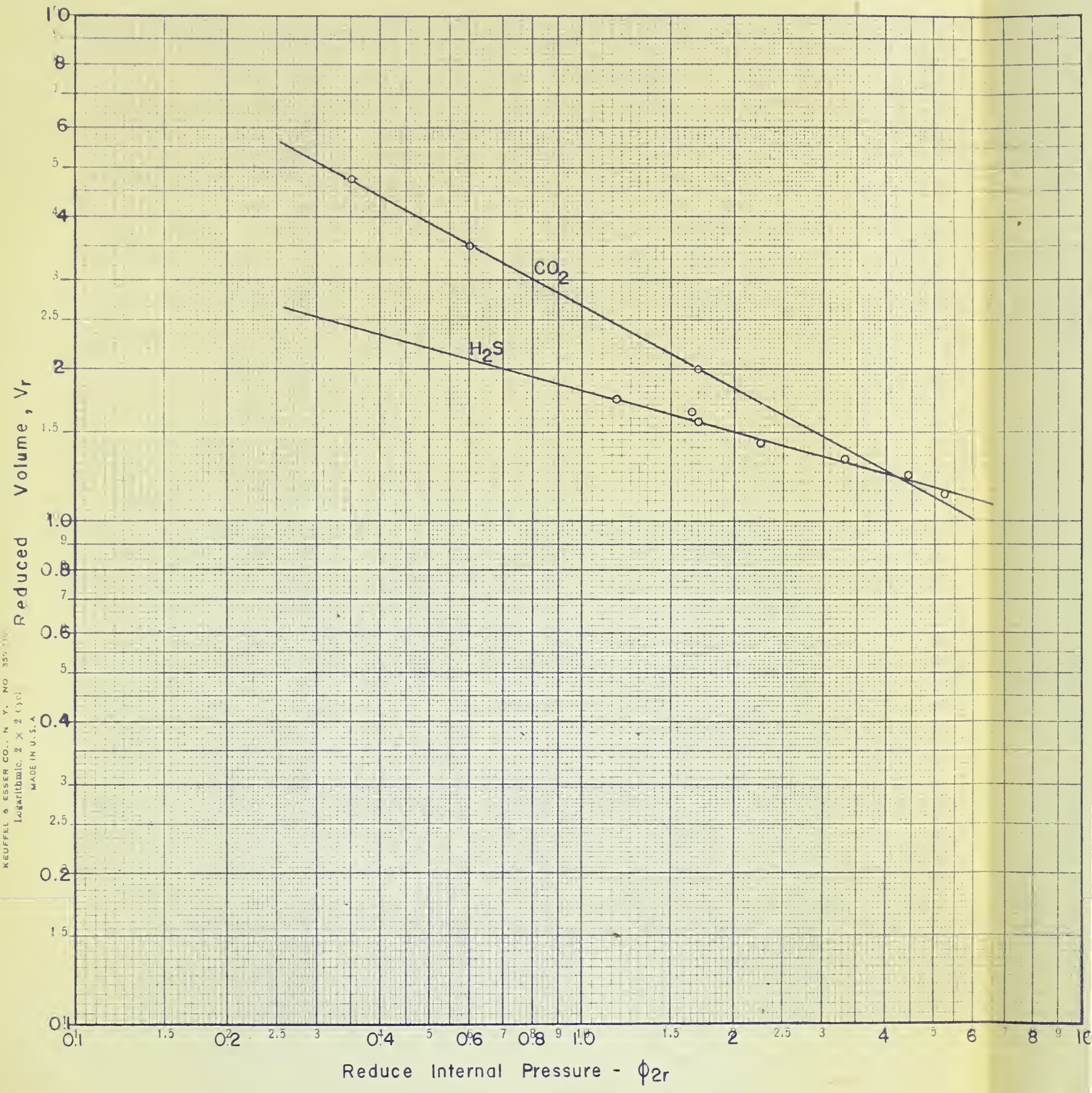

Figure-11 $V_r - \phi_{2r}$ Relationship for H_2S and CO_2

Substituting the values of P and ϕ_2 as found above in the equation for the binary mixtures:

$$P_{mix} = y_{CO_2}P_{CO_2} + y_{H_2S}P_{H_2S} + y_{CO_2}y_{H_2S}(\sqrt{\phi_{2CO_2}} - \sqrt{\phi_{2H_2S}})^2$$

we get: $V_1 = .1662$ or $z_1 = 0.4$

$$\begin{aligned} P_{mix} &= (.2)\times(62.2) + (.8)\times(98.6) + (.2)\times(.8)\times(\sqrt{(114)} - \sqrt{(158.4)})^2 \\ &= 12.54 + 78.68 + (.16)\times(10.68 - 12.55)^2 \\ &= 12.54 + 78.68 + (.16)\times(-1.87)^2 = 12.54 + 78.68 \\ &\quad + 0.56 = \underline{91.78} \text{ atm.} \end{aligned}$$

$V_2 = .2493$ or $z_2 = 0.6$

$$\begin{aligned} P_{mix} &= (.2)\times(58.7) + (.8)\times(78.1) + (.16)\times(\sqrt{26.7} - \sqrt{76.7})^2 \\ &= 11.74 + 62.48 + (.16)\times(5.16 - 8.80)^2 \\ &= 11.74 + 62.48 + (.16)\times(-3.64)^2 = 11.74 + 62.48 \\ &\quad + 0.58 = \underline{74.80} \text{ atm.} \end{aligned}$$

$V_3 = .3324$ or $z_3 = 0.8$

$$\begin{aligned} P_{mix} &= (.2)\times(56) + (.8)\times(64.2) + (.16)\times(\sqrt{1.4} - \sqrt{46.0})^2 \\ &= 11.2 + 51.36 + (.16)\times(3.06 - 6.78)^2 \\ &= 11.2 + 51.36 + (.16)\times(-3.72)^2 = 11.2 + 51.36 \\ &\quad + .595 = \underline{63.16} \text{ atm.} \end{aligned}$$

Plotting the assumed compressibility factors vs the as above calculated P_{mix} we finally find the compressibility factor at 1000 PSIA or 68.0 atm. for the system to be $z_{mix} = 0.710$.

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